I, Deborah H. Metz, hereby submit this original work as part of the requirements for the degree of Doctor of Philosophy in Environmental Science.

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The Effect of Natural Organic Matter on UV/H2O2 Treatment and the Effect of UV/H2O2 Treatment on Natural Organic Matter

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The Effect of Natural Organic Matter on UV/H₂O₂ Treatment and the Effect of UV/H₂O₂ Treatment on Natural Organic Matter

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by

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Abstract

Ultraviolet light with hydrogen peroxide (UV/H$_2$O$_2$) produces hydroxyl radicals that degrade organic micro-pollutants. However, radicals react non-selectively with natural organic matter (NOM). This research effort quantified the effect of NOM variation on the efficiency of UV/H$_2$O$_2$ contaminant destruction, explored the kinetics of hydroxyl radical/NOM reactions, determined the effect of UV/H$_2$O$_2$ on biofilm formation potential, measured UV/H$_2$O$_2$ impact on trihalomethane (TTHM) and haloacetic acid (HAA5) formation potential, and evaluated UV/H$_2$O$_2$ effects on TTHM speciation after chlorination. Granular activated carbon (GAC) adsorption was investigated to improve process efficiency and reduce by-product formation potential without creating brominated THM problems.

A year-long UV/H$_2$O$_2$ pilot study was conducted to study seasonal variations in NOM and multiple GAC breakthrough conditions. Pilot-scale reactors consistently achieved 80% atrazine degradation, allowing comparison of low pressure (LP) and medium pressure (MP) lamps for contaminant destruction efficiency and unintended by-product formation.

The effect of NOM on UV/H$_2$O$_2$ destruction of atrazine, metolachlor, methyl tert-butyl ether (MTBE), methylisoborneol, ibuprofen, gemfibrozil, and 17α-ethynylestradiol was evaluated. UV absorbance scans demonstrated changes in NOM from UV/H$_2$O$_2$ that increased under certain NOM conditions. As NOM increased, electrical energy per order (E$_{EO}$) requirements for contaminant destruction increased; requirements increased
similarly for all contaminants. UV/H$_2$O$_2$ followed by GAC eliminated the contaminants, throughout the year. LP lamps had lower E$_{EO}$ requirements than MP lamps.

UV/H$_2$O$_2$ destruction of MTBE was evaluated with bench-scale experiments using waters with varying NOM. Destruction and E$_{EO}$ values correlated well with specific-ultraviolet absorption for pilot-scale and bench-scale experiments. Changes in the kinetics of NOM/hydroxyl radical reactions were observed with different types of NOM.

Total assimilable organic carbon (AOC) concentration increased through UV/H$_2$O$_2$ by 14 to 33%, more with conventionally treated (CONV) reactor influent than with Post-GAC influent. The AOC concentration increases generated by MP and LP processes were similar. The *Spirillum* strain AOC increased through UV/H$_2$O$_2$ 50 to 65% due to formation of smaller more soluble compounds, e.g., organic acids. *Pseudomonas fluorescens* strain AOC concentration increased when CONV water served as pilot influent, but not when Post-GAC water was used. GAC effluent streams receiving UV/H$_2$O$_2$ pretreatment produced biofilms with greater heterotrophic plate counts than controls. The GAC effluent stream following the MP reactor produced the most viable biofilm.

Three-day simulated distribution system (SDS) TTHM concentration increased through the UV/H$_2$O$_2$ reactors (20 to 118%). Post-GAC reactor influent produced lower 3-day SDS TTHM concentration than CONV influent after UV/H$_2$O$_2$. Three-day SDS HAA5 concentration increased for CONV UV/H$_2$O$_2$ pilot influent, but not for Post-GAC influent. No difference in 3-day SDS DBP concentrations was observed between LP and MP processes. Brominated THMs are more toxic than chloroform, thus minimizing them is desirable. UV/H$_2$O$_2$ did not shift 3-day SDS THMs towards the brominated species.
UV/H₂O₂ increased the TTHM contribution of 3-day SDS chloroform by 7 to 13%, while 3-day SDS bromoform TTHM contribution decreased by 0.5 to 7%. GAC adsorption after UV/H₂O₂ insignificantly increased 3-day SDS bromoform concentration from 0.01 to 0.02 µmole/L.

UV/H₂O₂ can be used with GAC for excellent contaminant removal and minimal adverse effects.
Extended Summary

This research investigated the destruction of micro-pollutants by ultraviolet light hydrogen peroxide (UV/H$_2$O$_2$) advanced oxidation with granular activated carbon (GAC) being used to help reduce energy demand, provide a polishing step for contaminant reduction and to help control undesirable byproducts. However, at the center of the research was a fundamental understanding of how natural organic matter (NOM) interfered with the process and was transformed by the process. When utilities install new processes they must be aware of unintended consequences of the process change and how it will affect overall water quality. An in-depth understanding of the physical and chemical transformations and their ramifications is essential.

Chapter 1 describes the research motivation, ideas, objectives and challenges. UV/H$_2$O$_2$ is an emerging drinking water technology for the reduction of many synthetic organic contaminants and undesirable natural organic constituents. However, NOM can interfere with micro-pollutant reduction and may be transformed to produce problematic by-products. NOM in drinking water sources is at least an order of magnitude greater in concentration than most target synthetic organic contaminants. NOM affects the efficiency of the UV/H$_2$O$_2$ process in two ways: as a hydroxyl radical scavenger and as an absorber of UV radiation. If UV radiation is absorbed, direct photolysis of contaminants is reduced and fewer hydroxyl radicals are produced to accomplish advanced oxidation of contaminants. It is also important to evaluate NOM by-products and their impact on water quality. Biofilm formation potential and disinfection by-product formation potential should be assessed.
In the first part of the study, the effect of NOM on the UV/H\textsubscript{2}O\textsubscript{2} process was studied and a better understanding gained of the NOM/hydroxyl radical. This insight is crucial if the impacts of NOM are to be mitigated. The first objective was to explore the effect of varying organic quality on the destruction of contaminants using a UV/H\textsubscript{2}O\textsubscript{2} continuous flow pilot plant and determine whether GAC adsorption used before or after UV/H\textsubscript{2}O\textsubscript{2} could improve efficiency of contaminant reduction. Additionally, it was important to gain an understanding of the magnitude of the NOM transformation and its impact on contaminant degradation. The second objective was to evaluate the effect of NOM on target contaminant destruction, varying multiple water quality conditions so as to understand their impact on destruction efficiency and to better understand the kinetics of hydroxyl radical/NOM reactions. This portion of the research was accomplished by using a collimated beam unit and a commercialized kinetic model for the UV/H\textsubscript{2}O\textsubscript{2} process.

In the second part of the study UV/H\textsubscript{2}O\textsubscript{2} organic by-product formation was evaluated. The third objective was to evaluate the effect of UV/H\textsubscript{2}O\textsubscript{2} on biofilm formation potential and determine whether GAC adsorption used before or after UV/H\textsubscript{2}O\textsubscript{2} could reduce undesirable by-products. The fourth objective was to evaluate regulated trihalomethane and haloacetic acid formation potential through UV/H\textsubscript{2}O\textsubscript{2} and determine whether GAC adsorption used before or after UV/H\textsubscript{2}O\textsubscript{2} could reduce by-product potential. The fifth objective was to determine how UV/H\textsubscript{2}O\textsubscript{2} affects the speciation of trihalomethanes formed upon chlorination and how GAC adsorption used before or after UV/H\textsubscript{2}O\textsubscript{2} could impact this speciation. Speciation of chlorinated disinfection by-products can affect toxicity and regulatory compliance, and it is desirable to minimize brominated species.
Chapter 2 describes emerging organic contaminants, treatment technologies and pitfalls, current research and dissertation focus areas. Not only are water utilities facing concerns from traditionally troublesome natural organic contaminants such as methylisoborneol (MIB) and geosmin and regionally problematic occurrences of synthetic organic contaminants such as methyl tert-butyl ether (MTBE), but more recently trace contaminants of pharmaceutical and personal care products (PPCP) have been reported in technical and popular publications. While the concentrations are generally well-below therapeutic values, the synergistic effects, antibiotic resistance and the effects of lifetime exposures are unknown. This present study determined the destruction and removal efficiency of 7 compounds: atrazine, metolachlor, MTBE, MIB, ibuprofen, gemfibrozil, and ethynylestradiol. These compounds represent major emerging and problematic contaminant groups that are found to occur frequently. They vary in chemical formulas, bonds and structure of the compounds, solubility and second order reaction rate constant with the hydroxyl radical. They were spiked at environmentally relevant concentrations.

Researchers have shown varying effectiveness of drinking water treatment for removing organic micro-pollutants. Coagulation, sedimentation and filtration are ineffective for removing trace organic contaminants. While typically used drinking water oxidants can be useful in degrading trace level emerging contaminants, those oxidants that produced hydroxyl radicals were the more effective. UV/H$_2$O$_2$ was found to be very effective for the destruction of many of the emerging contaminants. Researchers have also found GAC to be effective in removing many of these contaminants.
The major thrust of this research was the study of UV/H$_2$O$_2$ destruction of contaminants, a deeper understanding of problems caused by UV/H$_2$O$_2$ reactions with NOM and conditions and treatments that minimize the undesired by-products. The effectiveness of GAC for removing trace organic contaminants was compared to UV/H$_2$O$_2$. The use of GAC before or after the process was evaluated for the reduction of undesirable by-products. Different states of GAC exhaustion were explored. The effect of biologically active GAC was also considered. The quantity and nature of NOM and the effect of NOM on the efficiency of the process was evaluated. The kinetics of the NOM-hydroxyl radical reaction additionally were explored. Various tools were used to understand the effect of this reaction. A number of techniques were used to assess the changes to NOM due to UV/H$_2$O$_2$ treatment and the effect on water quality: TOC/DOC, SUVA, UV$_{254}$ absorbance, UV scans from (200-400 nm), AOC, including the *Pseudomonas fluorescens* strain P17 and *Spirillum* strain NOX components, direction biofilm production by annular reactor and trihalomethane and haloacetic acid formation potential.

In Chapter 3 an understanding of the effect of NOM on the UV/H$_2$O$_2$ process was gained. This part of the study evaluated the effect of NOM on contaminant destruction by UV/H$_2$O$_2$. Seven contaminants were evaluated by UV pilot-scale experiments. UV scans collected before and after the reactors demonstrated the change in NOM due to radical attack. Methyl tert-butyl ether (MTBE) destruction by UV/H$_2$O$_2$ was evaluated using a bench-top collimated beam unit. To reflect different amounts and types of NOM in drinking water; conventionally treated (CONV) water, GAC treated (Post-GAC) water from a drinking water treatment plant and laboratory generated reverse osmosis (RO)
water were examined. Water with higher NOM concentration and humic content, required higher UV fluence (dose) and energy than water with lower NOM to achieve comparable results. Higher NOM resulted in a higher electrical energy per order ($E_{EO}$) requirement for UV/H$_2$O$_2$ target contaminant destruction. Higher NOM increased the $E_{EO}$ similarly for the seven compounds considered. LP lamps had lower $E_{EO}$ requirements than MP lamps. UV/H$_2$O$_2$ followed by GAC eliminated the contaminants, throughout the year. MTBE destruction correlated very well with the SUVA values. The $E_{EO}$ for MTBE destruction correlated well with SUVA for both the pilot-scale and bench-scale experiments. Insight was gained into the kinetics of the NOM hydroxyl radical reaction.

Chapter 4 explored the effect of UV/H$_2$O$_2$ on biofilm formation potential and whether GAC adsorption used before or after UV/H$_2$O$_2$ could reduce undesirable by-products. A year-long UV/H$_2$O$_2$ pilot study was conducted to examine a variety of seasonal and granular activated carbon (GAC) breakthrough conditions. The UV pilot-scale reactors were set to consistently achieve 80% atrazine degradation, allowing comparison of low pressure (LP) and medium pressure (MP) lamp technologies for by-product formation. Because hydroxyl radicals react non-selectively with organic compounds, unintended by-product formation occurred.

Total assimilable organic carbon (AOC) concentration increased through the reactors from 14 to 33% on average, depending on water quality. NOM contains the precursors for AOC production, so the lower NOM Post-GAC process stream produced less AOC than the CONV process stream. No appreciable difference in AOC concentration was observed between LP and MP UV reactors. The Spirillum strain NOX fraction of the AOC increased from 50 to 65% on average, depending on the quality of the water. The
increase in this fraction of AOC occurred because oxidation of NOM yielded smaller more assimilable organic compounds such as organic acids that are necessary for NOX growth. The *Pseudomonas fluorescens* strain P17 AOC concentration increased only when conventionally treated plant water was used as pilot influent. This organism thrives in waters of differing organic energy sources, but does not thrive well in carboxylic acids alone. The CONV water had more overall TOC that could contribute to higher P17 AOC counts. Biofilms with greater heterotrophic plate counts were observed in the granular activated carbon (GAC) effluent streams receiving UV/H₂O₂ pretreatment. Biofilm coupon studies additionally indicated that the effluent stream of the GAC column proceeded by the MP reactor exhibited more viable biofilm than the other GAC effluent streams based on an adenosine triphosphate (ATP) bioluminescence method. The increased viability of the biofilm produced by the MP UV reactor is likely a result of the multiple UV wavelengths and higher energy input characteristic of this technology.

Chapter 5 evaluated the regulated trihalomethane and haloacetic acid formation potential through UV/H₂O₂ and explored whether GAC adsorption used before or after UV/H₂O₂ could reduce by-product potential. Additionally, the effect of UV/H₂O₂ on the speciation of trihalomethanes formed upon chlorination was evaluated. GAC adsorption used before or after UV/H₂O₂ was examined relative to speciation. This study evaluated disinfection by-product (DBP) precursor formation for UV/H₂O₂ while reducing traces organic contaminants in natural water (> 90% for target pharmaceuticals, pesticides and taste and odor producing compounds and 80% atrazine degradation). Two process waters of differing quality were used as pilot influent, i.e., before and after granular
activated carbon adsorption. DBP precursors increased through UV/H₂O₂ under most of the conditions studied. Regulated trihalomethane formation potential increased through the UV/H₂O₂ reactors from 20 to 118%, depending on temperature and water quality. When Post-GAC water served as reactor influent, lower DBP concentrations were produced in comparison to CONV treated water. Three day simulated distribution system (SDS) haloacetic acid (HAA5) increased when conventionally treated water served as UV/H₂O₂ pilot influent, but only increased slightly when GAC treated water served as pilot influent. No difference in 3-day simulated distribution system DBP concentration was observed between LP and MP UV reactors when 80% atrazine degradation was targeted.

Chapter 6 presented the conclusions and recommendations of the dissertation. Some recommendations for future work include:

- Developing a better understanding of the chemical changes that occur with NOM upon UV/H₂O₂ treatment. This understanding will help researchers find ways to avoid the unintended consequences of these reactions and develop technologies to deal with the problems.

- Determining how to enhance biologically active carbon after UV/H₂O₂. Optimizing the removal potential of the GAC should make the combined process even more viable.

- Further exploring biofilm formation potential with biofilm annular reactors using the new ATP methodologies, verifying findings on the MP UV/H₂O₂ reactor effluent.
● Studying whether there are differences in the way the various wave lengths of the medium pressure lamp impact NOM.

● Continuing development of more efficient UV lamps or developing practical catalytic solutions that will reduce the energy use and carbon footprint of this technology.
Acknowledgments

I appreciate the guidance of Dr. Dionysios Dionysiou in my research. He has always challenged me to go deeper into the scientific understanding of my empirical data. He has helped focus my natural curiosity and given me the tools to answer the question: “why”. These tools will serve me well in my career. I have also gained a greater appreciation of how university and utility partnerships can achieve much and are instrumental in advancing the field.

I’d also like to thank my husband, Jerry, for his complete support and for handling many things around the house that I just didn’t have time to do. I’d also like to thank my children, Drew, Matt and Angie, for their love and support and their families Shannon, Rachel, Isaiah and Ryan who understood when I was sometimes absent.

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<tr>
<td>ADP</td>
<td>adenosine diphosphate</td>
</tr>
<tr>
<td>AMWD</td>
<td>apparent molecular weight distribution</td>
</tr>
<tr>
<td>AOC</td>
<td>assimilable organic carbon</td>
</tr>
<tr>
<td>ATP</td>
<td>adenosine triphosphate</td>
</tr>
<tr>
<td>BPA</td>
<td>bisphenol A</td>
</tr>
<tr>
<td>BDOC</td>
<td>biodegradable dissolved organic carbon</td>
</tr>
<tr>
<td>CCL3</td>
<td>USEPA contaminant candidate list</td>
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<tr>
<td>CONV</td>
<td>conventional treatment</td>
</tr>
<tr>
<td>DDT</td>
<td>dichloro diphenyl trichloroethane</td>
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<tr>
<td>DOC</td>
<td>dissolved organic carbon</td>
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<tr>
<td>DBP</td>
<td>disinfection by-product</td>
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<tr>
<td>E2</td>
<td>17 β-estradiol</td>
</tr>
<tr>
<td>EE2</td>
<td>17 α-ethynylestradiol</td>
</tr>
<tr>
<td>EBCT</td>
<td>empty bed contact time</td>
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<tr>
<td>EDC</td>
<td>endocrine disrupting compound</td>
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<tr>
<td>E&lt;sub&gt;E0&lt;/sub&gt;</td>
<td>Electrical energy per order of destruction</td>
</tr>
<tr>
<td>GAC</td>
<td>granular activated carbon</td>
</tr>
<tr>
<td>GCWW</td>
<td>Greater Cincinnati Water Works</td>
</tr>
<tr>
<td>HAA5</td>
<td>haloacetic acids regulated by USEPA</td>
</tr>
<tr>
<td>HPC</td>
<td>heterotrophic plate count</td>
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<td>LP</td>
<td>low-pressure</td>
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<tr>
<td>MCL</td>
<td>USEPA maximum contaminant level</td>
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<tr>
<td>MIB</td>
<td>methylisoborneol</td>
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<tr>
<td>MP</td>
<td>medium-pressure</td>
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<td>MTBE</td>
<td>methyl tert-butyl ether</td>
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<tr>
<td>MW</td>
<td>molecular weight</td>
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<tr>
<td>NOM</td>
<td>natural organic matter</td>
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<tr>
<td>NOX</td>
<td><em>Spirillium</em> strain NOX</td>
</tr>
<tr>
<td>P17</td>
<td><em>Pseudomonas fluorescens</em> strain P17</td>
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<table>
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<tr>
<th>Acronym</th>
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<tbody>
<tr>
<td>Post-GAC</td>
<td>GAC effluent after sand filtration</td>
</tr>
<tr>
<td>PPCP</td>
<td>pharmaceutical and personal care products</td>
</tr>
<tr>
<td>RLU</td>
<td>relative light units</td>
</tr>
<tr>
<td>RMTP</td>
<td>Richard Miller Treatment Plant</td>
</tr>
<tr>
<td>RO</td>
<td>reverse osmosis</td>
</tr>
<tr>
<td>SDS</td>
<td>simulated distribution system</td>
</tr>
<tr>
<td>SUVA</td>
<td>specific ultraviolet absorbance</td>
</tr>
<tr>
<td>TCA</td>
<td>trichloroacetic acid</td>
</tr>
<tr>
<td>TOC</td>
<td>total organic carbon</td>
</tr>
<tr>
<td>THM</td>
<td>trihalomethane</td>
</tr>
<tr>
<td>TTHM</td>
<td>Total trihalomethanes regulated by USEPA</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet light</td>
</tr>
<tr>
<td>UVA</td>
<td>Ultraviolet light absorbance</td>
</tr>
<tr>
<td>UV/H₂O₂</td>
<td>UV/hydrogen peroxide advanced oxidation</td>
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## List of Abbreviations

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<tr>
<th>Acronym</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>UVT\textsubscript{254}</td>
<td>ultraviolet transmittance at 254 nm</td>
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Chapter 1

Introduction to Dissertation Research
Ultraviolet light hydrogen peroxide (UV/H$_2$O$_2$) advanced oxidation is an emerging drinking water technology for the reduction of many synthetic organic contaminants and undesirable natural organic constituents. However, natural organic matter (NOM) can interfere with micro-pollutant reduction and may be transformed to produce problematic by-products. NOM in drinking water sources is at least an order of magnitude greater in concentration than most target synthetic organic contaminants. NOM affects the efficiency of the UV/H$_2$O$_2$ process in two ways: as a hydroxyl radical scavenger and as an absorber of UV radiation. If UV radiation is absorbed, direct photolysis of contaminants is reduced and less hydroxyl radicals are produced to accomplish advanced oxidation of contaminants. It is also important to evaluate NOM by-products and their impact on water quality. Biofilm formation potential and disinfection by-product formation potential should be assessed.

In the first part of the study an understanding was gained of the effect of NOM on the UV/H$_2$O$_2$ process. This insight is crucial if the impacts of NOM are to be mitigated. The first objective was to explore the effect of varying organic quality on the destruction of contaminants using a UV/H$_2$O$_2$ continuous flow pilot plant and determine whether GAC adsorption used before or after UV/H$_2$O$_2$ could improve efficiency of contaminant reduction. Additionally, it was important to gain an understanding of the magnitude of the NOM transformation and its impact on contaminant degradation. The second objective was to evaluate the effect of natural organic matter on target contaminant destruction, varying multiple water quality conditions so as to understand their impact on efficiency and to better understand the kinetics of the hydroxyl radical/NOM reaction. This portion of the research was accomplished by using a collimated beam unit and the AdOx™ model (Crittenden et al., 1999).

In the second part of the study NOM by-product formation from the UV/H$_2$O$_2$ process was explored. The third objective was to explore the effect of UV/H$_2$O$_2$ on biofilm formation potential and determine whether GAC adsorption used before or after UV/H$_2$O$_2$ could reduce undesirable by-products. The fourth objective was to evaluate regulated trihalomethane and haloacetic acid formation potential through UV/H$_2$O$_2$ and determine whether GAC adsorption used before or after UV/H$_2$O$_2$ could reduce by-product potential. The fifth objective was to evaluate how UV/H$_2$O$_2$ affects the speciation of trihalomethanes formed upon chlorination and how GAC adsorption used before or after UV/H$_2$O$_2$ could impact this speciation. Speciation of chlorinated disinfection by-products can affect toxicity and regulatory compliance, and it is desirable to minimize brominated species.
1. Introduction

1.1. Motivation and Rationale

*Need to better understand the role of NOM in the UV/H$_2$O$_2$ process and mitigate problems created*

Ultraviolet light hydrogen peroxide (UV/H$_2$O$_2$) advanced oxidation is a promising drinking water technology for the removal/elimination of a broad-spectrum of synthetic organic contaminants and undesirable natural organic constituents. UV/H$_2$O$_2$ combines direct photolysis and advanced oxidation through indirect photolysis for the destruction of organic compounds in water (Pereira et al., 2007). However, natural organic matter (NOM) can interfere with micro-pollutant removal and may be transformed to produce problematic by-products.

NOM in drinking water sources is at least one order of magnitude greater in concentration than most target synthetic organic contaminants. NOM affects the efficiency of the UV/H$_2$O$_2$ process in two ways: as a hydroxyl radical scavenger and as an absorber of UV radiation. If UV radiation is absorbed, direct photolysis of contaminants is reduced and a lower quantity of hydroxyl radicals are produced to accomplish advanced oxidation of contaminants. It is also important to evaluate NOM degradation products and their impact on water quality. Upon UV/H$_2$O$_2$ treatment, researchers have noted a reduction in NOM aromaticity (Thomson et al., 2004, Kleiser and Frimmel, 2000, Toor and Moseni, 2007 and Sarathy and Mohseni, 2007 and 2010), a shift to smaller molecular size (Sarathy and Mohseni, 2009), the creation of more biodegradable compounds (Thomson et al., 2004, Toor and Mohseni 2007, Sarathy and Mohseni, 2009) and a decrease in hydrophobicity (Sarathy and Mohseni, 2009 and
These changes could lead to undesirable by-products, but may be able to be improved by the use of GAC. These changes may also lead to increased bioactivity on the GAC and enhance biologically active granular activated (GAC) treatment after UV/H₂O₂ reactors, helping to reduce NOM by-products.

1.1.1. Proposal Idea I: Explore the effect of varying organic quality on the destruction of contaminants by UV/H₂O₂ and whether GAC used before or after UV/H₂O₂ can improve efficiency of contaminant removal.

The efficiency of the UV/H₂O₂ process is dependent upon the rate of formation of hydroxyl radicals, UV absorbance by treated water and the concentration of hydroxyl radical scavengers. UV absorbance by the process water varies with the type and concentration of dissolved matter, particularly NOM (Antoniou et al., 2009). The most prominent hydroxyl radical scavengers are alkalinity (HCO₃⁻, CO₃²⁻) and dissolved NOM (Pereira et al., 2007). NOM diminishes the efficiency of the UV/H₂O₂ process in two ways: by absorbing UV radiation and acting as a hydroxyl radical scavenger. The fraction of UV radiation photons absorbed by NOM, it is unavailable to degrade micro-pollutants by photolysis and is unavailable to convert H₂O₂ into hydroxyl radicals needed for contaminant destruction by advanced oxidation. Higher UV and hydrogen peroxide doses must be applied to compensate for UV radiation absorption and hydroxyl radical scavenging by NOM (He, et al., 2011). Thus, waters with high NOM concentrations generally require a greater capital investment and higher operating costs than low NOM waters to achieve similar destruction of contaminants by UV/H₂O₂. Therefore, it is important to understand how NOM reacts under these circumstances.
and to determine the kinetics of those reactions in order to properly design efficient UV/H$_2$O$_2$ systems.

Drinking water sources vary in the type and amount of NOM present, and significant seasonal variations are usual for surface water sources. Additionally, the UV/H$_2$O$_2$ process can be inserted into the treatment plant at various points in the treatment process (Ijpelaar et al., 2010). For instance, GAC adsorption is beneficial in reducing NOM, particularly UV$_{254}$ absorbable materials, high molecular weight compounds and hydrophobic NOM. When GAC is employed before the UV/H$_2$O$_2$ reactors, a lower UV absorbance may lead to better process efficiency. When GAC adsorption follows the UV/H$_2$O$_2$ process, the GAC may remove degradation by-products and excess H$_2$O$_2$. By understanding the effect of various types of NOM on the UV/H$_2$O$_2$ process and understanding the kinetics of those reactions, more efficient and cost effective installations can be designed.

The UV/H$_2$O$_2$ process is a very energy intensive process, and the energy consumption should be considered when determining up-stream processes or lamp technology. A fundamental measurement of the energy efficiency of a UV advanced oxidation system is the Electrical Energy per Order (E$_{EO}$). It is defined as “the number of kilowatt-hours of electrical energy required to reduce the concentration of a contaminant by one order of magnitude in a specified volume of water”, i.e., 1,000 L (Sharpless et al., 2005). Understanding the relationship of NOM to E$_{EO}$ is critically important to system design. Both bench and pilot plant studies can be performed to assess the effect of NOM on process efficiency. Based on the results of preliminary bench experiments, two commonly used types of UV lamp technologies were compared with operational
parameters set to achieve consistent contaminant degradation. The pilot-scale system was operated for a year, measuring the effects of NOM seasonality on process efficiency. The difference in efficiency between a conventionally treated (CONV) UV/H\textsubscript{2}O\textsubscript{2} pilot reactor influent and a Post-GAC pilot reactor influent was assessed for the destruction of seven trace organic contaminants. Bench-scale collimated beam experiments added to the understanding of how NOM affects UV/H\textsubscript{2}O\textsubscript{2} by providing a more controlled environment to test a range of degradation and UV doses. Crittenden et al. (1999) developed an AdOx™ model that can be used to better understand the kinetics of the hydroxyl radical reaction with NOM and the target contaminant. This can be used to better understand hydroxyl radical formation, reaction rates for the target contaminant and the reaction rate of NOM.

This UV/H\textsubscript{2}O\textsubscript{2} pilot-scale study was unique because it was designed to examine a variety of seasonal and granular activated carbon (GAC) breakthrough conditions. The UV pilot-scale reactors were set to achieve a consistent degradation of chemical micropollutants, allowing comparison of low pressure (LP) and medium pressure (MP) lamp technologies for destruction of multiple contaminants relative to one another. Atrazine was used to determine the operational conditions of the UV/H\textsubscript{2}O\textsubscript{2} pilot plant. The pilot-scale facility conditions were set to consistently achieve 80 percent atrazine reduction. As shown in preliminary tests, the major mechanism of destruction for atrazine was the hydroxyl radical reaction. This normalized condition allowed for comparison of the technologies using performance–based data. The effects of NOM effects could be studied and compared under these normalized conditions. Since the ultraviolet transmittance at wavelength 254 nm (UVT\textsubscript{254}) and total organic carbon (TOC)
concentration of the water varied seasonally, routine analyses and calibrations were necessary.

No other researchers have taken this approach. The study combined the practicality of real world conditions at a drinking water treatment plant with fundamental analysis of the results. The collimated beam bench tests complemented the pilot work and allowed for the assessment of more water quality and reagent variables. GAC treatment before the UV/H$_2$O$_2$ process was expected to decrease the scavenging effect of NOM depending on the organic loading on the GAC. Relationships between electrical input and destruction efficiency were established and additional insights into the kinetics of the NOM-hydroxyl radical reaction were gained.

1.1.2. Proposal Idea II: Explore the effect of UV/H$_2$O$_2$ on biofilm formation potential and whether GAC used before or after UV/H$_2$O$_2$ can reduce undesirable by-products.

Distribution system biofilm growth is caused by a combination of factors. Generally, four water quality parameters control microbial regrowth: temperature, assimilable organic carbon (AOC), availability of nutrients (trace inorganic compounds) and residual disinfectant presence (Reasoner et al., 1991). Kaplan et al., (2004) determined that source waters possess widely different quantities and qualities of biodegradable organic as carbon sources, and these differences in organics influence the quantity and type of biofilm. It is well known that that ozone treatment can increase AOC concentration. An assumption of this work was that UV/H$_2$O$_2$ process would also increase biodegradability of NOM, enough to cause detrimental water quality changes, but that GAC would help to sufficiently improve the water quality. This proved to be the case.
Biodegradable organics leaving the drinking water plant can cause microbial regrowth in the distribution system, a potentially serious problem. Weinrich et al., (2009) states that “In distributed water, bacterial regrowth is perhaps the most significant mechanism for water quality deterioration between the treatment plant and the end user.” Coliform bacteria and pathogenic organisms can grow and be shielded in the biofilm and be difficult to eliminate. Biofilms can be responsible for disinfectant depletion and problems with taste and odor. In chloraminated systems nitrification may also occur. Even corrosion rate can be increased by the presence of biofilm under certain conditions (Geesey et al., 1989).

The UV/H$_2$O$_2$ process forms hydroxyl radicals that react non-selectively with NOM as well as the target contaminants. Organic free radicals then can form small MW fractions such as aldehydes, ketones, alcohols, and carboxylic acids that can be used in microbial metabolism. Acetic and oxalic acids are often found as intermediates of the NOM oxidation process, and these acids biodegrade readily (Speitel et al., 1999).

Thomson et al., (2004), Toor and Mohseni (2007) and Sarathy and Mohseni, (2009) found that UV/H$_2$O$_2$ can increase the quantity of biodegradable compounds, and others have noted a decrease in hydrophobicity (Sarathy and Mohseni, 2009 and 2010) that could lead to the production of compounds more assimilable by micro-organisms.

Assimilable organic carbon (AOC) is one of the methods used to assess biofilm formation potential and the class of compounds causing the problem. The AOC test has been found to be a useful tool for predicting bacterial growth in the distribution system.
In this study, seasonal variations in AOC were assessed by collecting quarterly AOC samples.

Annular reactors can be used to directly assess biofilm potential after GAC adsorption in process streams as per Sharp et al., (2001). This method is more sensitive than the AOC method and gives “real-time” results. This methodology can be used to test differences among the final process waters. For this work a bioluminescent method for biofilm quantification was developed and compared to an older standard plate count method for this assessment.

Based on preliminary bench experiments, The biofilm potential produced by two types of UV lamps (MP and LP) was compared using pilot reactors with operational parameters set to achieve a consistent contaminant reduction. Biofilm potential was assessed over a year of pilot plant operation, measuring the effects of NOM seasonality on AOC and biofilm formation. The difference in biofilm potential between a conventionally treated UV/H₂O₂ pilot reactor influent and a Post-GAC pilot reactor influent was assessed. It was determined that GAC could mitigate increases in biofilm potential after UV/H₂O₂. Two AOC methodologies and a biofilm coupon method using a direct count and a unique bioluminescence method developed specifically for this research were employed. These techniques added to the understanding of how UV/H₂O₂ promotes bacterial growth. Additionally, the bioactivity of the GAC was monitored for improvements in NOM removal due to the formation of assimilable organic compounds through the UV/H₂O₂ process. Additional improvements were expected during the warmer weather. Improvements had been noted by previous
investigators, but were not able to be quantified in a continuously operated pilot-scale unit with normalized practical contaminant destruction.

This UV/H$_2$O$_2$ pilot-scale study of biofilm potential was unique because it was conducted over a full year to examine a variety of seasonal and GAC breakthrough conditions. Again, the UV pilot-scale reactors were set to achieve a consistent degradation of chemical micro-pollutants, allowing comparison of low pressure (LP) and medium pressure (MP) lamp technologies for by-product formation. Both commonly recognized components of the assimilable organic carbon (AOC) were assessed in order to better understand the changes in water chemistry responsible for increased biofilm formation potential and improved biologically active GAC treatment. This gave more fundamental insight into the types of compounds that were being transformed. This was a novel approach. Biofilm formation potential was also assessed by on-line annular reactors that simulated distribution pipe conditions. One enumeration method used was an ATP bioluminescence method (specifically developed for this research). By this method both the quantity and viability of the biofilm was assessable. The unique approach of the study allowed subtle differences in water quality to be explored relative to biofilm potential and an understanding of the types of compounds responsible for these differences.

1.1.3. Proposal Idea III: Explore effect of UV/H$_2$O$_2$ on disinfection by-product formation potential and whether GAC used before or after UV/H$_2$O$_2$ can reduce undesirable by-products.

Several researchers have studied the reduction of NOM and DBP precursors through UV/H$_2$O$_2$. Matilainen and Sillanpää (2010) and Bond, et al. (2011) have published
comprehensive review articles that summarize this NOM (2010) and DBP (2011) formation potential research to date. A few researchers have found that at lower more practical UV/H$_2$O$_2$ conditions small increases in DBP formation potential could occur (Kleiser and Frimmel, 2000, Toor and Moseni, 2007, Dotson et al., 2010 and Sarathy and Mohseni, 2010), but no long-term comprehensive study has been performed that considers seasonal variations in water quality with the combination of UV/H$_2$O$_2$ and GAC.

The United States Environmental Protection Agency (USEPA) has promulgated the Disinfectants/Disinfection By-product Rule (USEPA, 2006) setting maximum contaminant levels (MCLs) for the sum of four trihalomethanes (TTHM) and the sum of five haloacetic acids (HAA5) at 0.080 mg/L and 0.060 mg/L, respectively. This Rule required compliance to be determined on an annual running average of multiple locations. The Stage II Rule was implemented for many systems in 2012 and will require that each sampling location comply with the MCLs. In 2005 the World Health Organization set acute guidelines for the individual THMs emphasizing the varying toxicity of these compounds. The guideline for chloroform was set at 300 µg/L, bromodichloromethane at 60 µg/L, dibromochloromethane at 200 µg/L and bromoform at 100 µg/L.

Based on preliminary bench experiments, the DBP formation potential produced by two types of UV lamps (MP and LP) was compared using pilot reactors with operational parameters set to achieve a consistent contaminant degradation. DBP formation potential was assessed over a year of pilot plant operation, measuring the effects of NOM seasonality on TTHM and HAA5 formation potential. The DBP formation potential
difference between a conventionally treated UV/H₂O₂ pilot reactor influent and a Post-
GAC pilot reactor influent was explored. It was determined that GAC could mitigate 
increases in DBP formation potential when used before or after UV/H₂O₂. The TTHM 
and HAA5 formation potential was evaluated using a 3-day simulated distribution 
system method developed specifically for this research. DBP speciation was studied 
through the unit processes to gain insight into DBP formation and potential remedial strategies.

This UV/H₂O₂ pilot-scale study of disinfection by-product formation potential was novel 
because it was performed under the same unique pilot conditions described above. This 
allowed for the comparison of the two lamp types and the varying qualities of water for 
disinfection by-product formation potential. Other studies have compared LP and MP 
lamps for NOM transformation at equal UV doses (Dotson et al., 2010 and Magnuson et 
al., 2002), but none have used the performance level approach. Distribution conditions 
were simulated to determine whether higher temperatures created greater differences in 
formation potential relative to controls. The use of GAC before or after the UV/H₂O₂ 
process also was a unique approach. Because GAC is known to preferentially reduce 
certain types of contaminants and increase brominated disinfection by-products, the 
study presented a unique opportunity to gain an understanding of the UV/H₂O₂ and how 
the two processes worked together. No other researchers have taken this same 
approach.

1.2. Objectives and Challenges

In order to develop the ideas mentioned above, five research objectives were adopted. 
These research objectives were divided into two parts. The first part deals with how the
reaction of hydroxyl radicals with NOM impacts the efficiency of the UV/H$_2$O$_2$ degradation process and determine the kinetics of the NOM-hydroxyl radical reaction. The second part deals with how the UV/H$_2$O$_2$ process transforms the NOM, focusing on biofilm formation potential and disinfection by-product formation potential. The objectives and some challenges associated with those objectives are described below.

1.2.1. Enhance Understanding of the Effect of NOM on the UV/H$_2$O$_2$ Process in Order to Gain Insight into How NOM Impacts can be Mitigated

This part of the study has two main objectives:

**Objective I. Explore the effect of varying organic quality on the destruction of contaminants using a UV/H$_2$O$_2$ continuous flow pilot plant and determine whether GAC adsorption used before or after UV/H$_2$O$_2$ can improve efficiency of contaminant reduction.**

The first objective was to explore the effect of varying organic content on the destruction of contaminants using a UV/H$_2$O$_2$ continuous flow pilot plant and determine whether GAC adsorption used before or after UV/H$_2$O$_2$ could improve efficiency of contaminant reduction. A continuous flow pilot facility provided the best opportunity to study seasonal variations of NOM and develop GAC breakthrough curves (after UV/H$_2$O$_2$) using pilot columns that followed the UV/H$_2$O$_2$ reactors. UV absorbance scans (200 - 300 nm) were used to understand the alteration of NOM through the process. Electrical usage was captured and $E_{EO}$ values were calculated. When GAC was used before the UV/H$_2$O$_2$ process, it reduced greater than 50% of NOM, but most readily removed large molecular weight non-polar organic compounds. These compounds absorbed UV$_{254}$ and reduced UV/H$_2$O$_2$ efficiency, so expectations were confirmed that GAC before UV/H$_2$O$_2$
appreciably improved UV/H\textsubscript{2}O\textsubscript{2} efficiency. As GAC became spent these compounds increased in the GAC effluent and heavy organic loading was experienced during some seasons. Therefore, the benefit of the GAC prior to UV/H\textsubscript{2}O\textsubscript{2} varied. GAC pilot columns used after UV/H\textsubscript{2}O\textsubscript{2} demonstrated that there was an advantage to using the two technologies in series and the GAC alone will produced acceptable results for most contaminants. Keeping the target contaminant (atrazine) destruction constant year-round was difficult due to changing organic quantity and type. However, when the influent organics were monitored closely, this goal was achievable.

**Objective II.** Evaluate the effect of natural organic matter on target contaminant destruction, varying multiple water quality conditions so as to understand their impact on efficiency.

The second objective was to evaluate the effect of natural organic matter on target contaminant destruction, varying multiple water quality conditions so as to understand their impact on efficiency and the kinetics of the NOM reaction. Although, the pilot-scale reactors were excellent for studying continuous processes in parallel and in series, they did not work as well for analyzing multiple variables in a rigorous fashion. A well-calibrated UV collimated beam unit allowed much flexibility in changing variables and gaining a better understanding of how different types of NOM compounds and inorganic constituents (such as pH and alkalinity) impact process efficiency and whether increasing the UV intensity or the H\textsubscript{2}O\textsubscript{2} concentration. The effluent waters from individual full-scale GAC contactors were able to be used to simulate a wide range of NOM conditions. These investigations were used to supplement the pilot results and gain more fundamental knowledge. The AdOx™ model developed by Crittenden et al.,
(1999) was used in conjunction with these bench-scale experiments to gain insight into hydroxyl radical formation and the kinetics and the reaction between NOM and the hydroxyl radical.

1.2.2. **Explore the Potential of Natural Organic By-product Formation through UV/H₂O₂.**

This part of the study had three main objectives:

**Objective III.** *Explore the effect of UV/H₂O₂ on biofilm formation potential and whether GAC adsorption used before or after UV/H₂O₂ can reduce undesirable by-products.*

The third objective was to explore the effect of UV/H₂O₂ on biofilm formation potential and determine whether GAC adsorption used before or after UV/H₂O₂ could reduce undesirable by-products. The increase in biofilm potential through the UV/H₂O₂ process was assessed. AOC concentration and direct biofilm measurement were used to determine whether the processes increase or decrease biofilm potential. The increased bioactivity in the GAC following UV/H₂O₂ was also evaluated through chemical and microbiological analyses to determine if any improvements in organic removal were observed. Total organic carbon, AOC, absorbance at UV₂₅₄, and specific UV absorbance at wavelength 254 nm (SUVA) was used to gain insight into the types of NOM compounds present through the unit processes. A new direct method for quantifying biofilm was developed using continuous flow annular reactors with biofilm coupons. Both heterotrophic plate count and adenosine triphosphate determinations were used to quantify bacterial density and cell viability.
**Objective IV.** Evaluate trihalomethane and haloacetic acid formation potential through \( UV/H_2O_2 \) and whether GAC adsorption used before or after \( UV/H_2O_2 \) can reduce by-product potential.

The fourth objective was to evaluate trihalomethane and haloacetic acid formation potential through \( UV/H_2O_2 \) and determine whether GAC adsorption used before or after \( UV/H_2O_2 \) could reduce by-product formation potential. A three day simulated distribution system method was developed to produce a realistic determination of disinfection by-product formation potential. GAC treatment was evaluated and significantly improved quality when used both before the \( UV/H_2O_2 \) process and after the \( UV/H_2O_2 \) when conventionally treated (CONV) water was used as pilot influent. A challenge was to end the three-day hold with a chlorine concentration that reflected realistic distribution system concentrations. This was particularly challenging because the excess \( H_2O_2 \) needed to be quenched on a stoichiometric basis, leaving no \( H_2O_2 \) to react with the chlorine. Careful measurements of chlorine, chlorine demand and residual \( H_2O_2 \) were made.

**Objective V.** Evaluate how \( UV/H_2O_2 \) affects the speciation of trihalomethanes formed upon chlorination and how GAC adsorption used before or after \( UV/H_2O_2 \) can impact this speciation.

The fifth objective was to evaluate how \( UV/H_2O_2 \) affects the speciation of trihalomethanes formed upon chlorination and how GAC adsorption used before or after \( UV/H_2O_2 \) can impact this speciation. It is commonly known that ozonation and GAC adsorption can produce a reduction in total THMs (upon chlorination), but an increase in
the percentage of brominated THMs. This was the case in this present study. As was mentioned previously, the brominated THMs have greater toxicity than chloroform. Also, the brominated THMs have a higher molecular weight. This is important from a regulatory standpoint because for regulatory purposes THMs are simply summed on a milligram per liter concentration basis. The total THM data will be analyzed from both a molar summation and a mass concentration summation and the change in bromine incorporation evaluated. It was not expected that UV/H₂O₂ would oxidize the natural bromide to hypobromous acid and cause higher bromine incorporation. This hypothesis was found to be true in the present study. However, it was expected that the use of GAC before or after UV/H₂O₂ would result in additional bromine incorporation upon chlorination and this also was the case. Because the UV/H₂O₂ process increased the THM formation potential, the shift to the more brominated species made a larger difference in the total THM concentration. While GAC used before or after UV/H₂O₂ reduced the quantity of DBP precursors, some of the brominated DBPs were increased by GAC adsorption.

1.3. References


Chapter 2

Emerging Organic Contaminants, Treatment Technologies and Pitfalls: Current Research and Dissertation Focus Areas
Not only are water utilities facing concerns from traditionally troublesome natural organic contaminants such as methylisoborneol (MIB) and geosmin and regionally problematic occurrences of synthetic organic contaminants such as methyl tert-butyl ether (MTBE), but more recently trace contaminants of pharmaceutical and personal care products (PPCP) have been reported in technical publications and mass media. While the concentrations are generally well-below therapeutic values, the synergistic effects, antibiotic resistance and the effects of lifetime exposures are unknown. This present study determined the destruction and removal efficiency of 7 compounds, atrazine, metolachlor, MTBE, MIB, ibuprofen, gemfibrozil, and ethynylestradiol (EE2). These compounds represent major emerging and problematic contaminant groups that are found to occur frequently. They vary in chemical formulas, bonds and structure of the compounds, solubility and second order reaction rate constant with the hydroxyl radical. They were spiked at environmentally relevant concentrations.

Researchers have shown varying effectiveness of drinking water treatment. Coagulation, sedimentation and filtration are ineffective for removing trace organic contaminants. While typically used drinking water oxidants can be useful to degrade trace level emerging contaminants, those that produced hydroxyl radicals were the more effective. UV/H$_2$O$_2$ was found to be very effective for the destruction of a many of the emerging contaminants. Researchers have also found GAC to be effective in removing many of these contaminants.

The major thrust of this research was to study UV/H$_2$O$_2$ destruction of contaminants, obtain a deeper understanding of problems caused by UV/H$_2$O$_2$ reactions with NOM and identify conditions and treatments that minimize the formation of undesired by-products. The effectiveness of GAC for removing trace organic contaminants was compared to UV/H$_2$O$_2$ and determined whether GAC used before or after the process could reduce undesirable by-products. Different states of GAC exhaustion were explored. The effect of biologically active GAC was also considered. The quantity and nature of NOM and the effect of NOM on the efficiency of the process were considered. The kinetics of the NOM-hydroxyl radical reaction additionally were explored. Various tools were used to understand the effect of this reaction. A number of techniques were used to assess the changes to NOM as a result of treatment and the effect on water quality: TOC/DOC, SUVA, UV254 absorbance, UV scans from (200-400 nm), AOC, including the Pseudomonas fluorescens strain P17 and Spirillum strain NOX components, direct measurement of biofilm production by annular reactor and trihalomethane and haloacetic acid formation potential.
2. Emerging Organic Contaminants, Treatment Technologies and Pitfalls: Current Research and Dissertation Focus Areas

2.1. Emerging Trace Organic Contaminants

Not only are water utilities facing concerns from traditionally troublesome natural organic contaminants such as methylisoborneol (MIB) and geosmin and regionally problematic occurrences of synthetic organic contaminants such as methyl tert-butyl ether (MTBE), but more recently trace contaminants of pharmaceutical and personal care products (PPCP) have been reported in technical and popular publications. However, these findings are not new. In the 1930s and 1940s scientists first noted that some synthetic compounds could mimic natural endocrine hormones in animals. These chemicals were identified as endocrine disruptors (EDCs) and included a variety of compounds, which could block the natural estrogen, testosterone and thyroidal hormones in animals, resulting in reproductive problems in many aquatic wildlife species (Walker and Janney, 1930 and Stroud 1940). In the middle of the twentieth century dichloro diphenyl trichloroethane (DDT) was shown to be an endocrine disrupting chemical (Bitman et al., 1968) and later found to exhibit teratogenic effects (Guillette, et al., 1994). Researchers have investigated EDCs in the US waters since the 1960s (Stumm-Zollinger, 1965 and Tabak and Bunch, 1970), and estrogenic impacts of wastewater containing EDCs have been observed (Routledge et al., 1998). Examples of EDCs with well-documented endocrine disruptive activity are DDT, atrazine, and 17 α- ethynyl estradiol (EE2), while broader groups include steroid hormones, alkylphenols, phthalates and phytoestrogens (Snyder et al., 2008). Another group of environmental contaminants, which cause
customer concern and may have human health effects, is the pharmaceuticals and personal care products (PPCPs). This category includes a variety of compounds such as antibiotics, antiseptics, medical contrast material, surfactants, heart medications and analgesics. They enter the environment through wastewater discharges, animal feeding operations, agricultural runoff and groundwater contamination. As the sensitivity of analytical instrumentation improves, the detection of many groups of compounds is now possible at trace levels. The range of concentrations of these micro-pollutants in U.S. waters varies between non-detectable and up to 20 µg/L (atrazine) with most contaminant concentrations being in the ng/L range (Snyder et al., 2007). A number of studies have found trace detections of these compounds in finished drinking water. Stackelberg et al. (2004), found 17 PPCPs in finished water systems. Phthlate esters have also been reported in finished water (Luks-Betlej et al., 2001 and Psillikis, et al., 2003). Herberer (2001) found clofibric acid, propylphenazine and diclofenac in finished drinking water. While the concentrations are generally well-below therapeutic values, the synergistic effects, antibiotic resistance and the effects of lifetime exposures are unknown.

This present study will determine the destruction and removal efficiency of 7 compounds, atrazine, metolachlor, MTBE, MIB, ibuprofen, gemfibrozil, and EE2. These compounds represent major emerging and problematic contaminant groups that are found to occur frequently. They vary in chemical formulas, bonds and structure of the compounds, solubility and second order reaction rate constant with the hydroxyl radical. They were spiked at environmentally relevant concentrations.
2.2. Treatment Technologies to Remove Emerging Trace Organic Contaminants

2.2.1. Coagulation, Sedimentation and Filtration

Because trace organic contaminants are diverse in chemical composition, no treatment technology provides the technological solution to all contaminants. Conventional treatment (before disinfection) mainly employs physical processes which are of limited value in reducing trace organic contamination. Ternes, et al., (2002) observed no significant reduction of four selected pharmaceutical compounds through coagulation/sedimentation or filtration. El-Dib and Aly (1977) found no reduction in phenylamide pesticides through conventional treatment. Seven common antibiotics: carbadox, sulfachlorpyridazine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfathiazole, and trimethoprim were not effectively removed in Missouri River water by conventional treatment (Adams, et al., 2002). Kim et al. (2007) found that conventional treatment was ineffective for 25 PPCPs found in surface waters and wastewater treatment. Westerhoff et al. (2005) spiked 62 compounds into natural waters and found some removal of the polyaromatic hydrocarbons through sorption on to solids, but the removal was < 25% for the other PPCPs/EDCs bench tested. Overall, coagulation, sedimentation and filtration are very ineffective for removing trace organic contaminants.

2.2.2. Traditional Oxidation

Chlorine has been used to reduce the concentration of some trace contaminants, but intermediates and chlorinated disinfection by-products must be monitored. Lee et al., (2004) studied the effect of chlorination on the elimination of three estrogenic chemicals such as 17 β-estradiol, nonylphenol and bisphenol. The indicated that the estrogenic
activity of these endocrine disruptors was significantly reduced as a result of chlorination. Pinkston and Sedlak (2004) found that the pharmaceutical contaminants studied reacted rapidly with free chlorine and would be transformed under the conditions typically encountered in many chlorine disinfection systems. The rate of transformation for compounds containing aromatic ether functional groups was strongly affected by the initial degree and type of ring substitution. The amine-containing pharmaceuticals rapidly reacted with the chlorine to form chlorinated amines. The chlorinated amines slowly decomposed to form species that could not be converted back into the parent compound. Alum, et al., (2004) found that both chlorination and ozonation effectively removed trace contaminant compounds spiked into distilled water (75% to 99%). As would be expected, increasing contact time and oxidant concentration improved compound removal. Chlorination by-products of bisphenol A (BPA), 17β-estradiol (E2), and EE2 resulted in low levels of estrogenicity over an extended period of time. For equivalent molar oxidant dosages, ozone and chlorine had comparable persistent estrogenicity and a greater than 99% loss of the parent compounds. However, oxidation with ozone was more rapid, reaching a stabilized estrogenic level in 10 min, while it took more than 120 min for the estrogenicity to stabilize in the chlorinated samples. Ternes (2003) reduced 25 PPCPs by applying 10–15 mg/L ozone with a contact time of 18 min. All of the pharmaceuticals investigated, as well as musk fragrances and estrone, were no longer detectable. Huber et al., (2003) found ozonation a promising process for an efficient destruction of nine pharmaceuticals in drinking waters. The selected pharmaceuticals were degraded about two to three times faster than other important trace contaminants such as MTBE and atrazine. Zwiener and
Frimmel (2000) studied the lipid lowering agent clofibric acid and the analgesic agents ibuprofen and diclofenac using ozone and ozone/hydrogen peroxide. Under study conditions, only diclofenac was degraded by ozone (97%). However, the combined application of ozone and hydrogen peroxide led to enhanced hydroxyl radical formation that improved the degradation efficiency of all investigated compounds. While typically used drinking water oxidants can be useful to degrade trace level emerging contaminants, those that produced hydroxyl radicals were the most effective. However, careful attention must be paid to oxidation by-products of all oxidants.

2.2.3. GAC Adsorption of Trace Organic Contaminants

Granular activated carbon (GAC) can be an effective treatment for emerging organic contaminants, but removal is dependent upon the type of GAC, empty bed contact time and the hydraulic and organic loading of the GAC and the characteristics of the target organic compound. Historically, granular GAC has been used for the adsorption of many organic compounds in drinking water. Initially it was used primarily for taste and odor control, later for the removal of specific organic contaminants and for disinfection by-product control. GAC is an effective adsorbent primarily due to its porous nature. Activated carbon pores have been divided into three size classifications: micropores (pore radius <1 nm), mesopores (pore radius > 1 nm and < 25 nm) and macropores (pore radius >25 nm). The various pore sizes serve different roles in adsorption. Pore size can also affect the degree of adsorption under oxic conditions (Lu and Sorial 2004). An important mechanism for organics removal by GAC is the chemical properties of the pore surfaces. Oxygen containing compounds dominate the functional groups and display both acidic and basic characteristics. In general, less soluble organic
compounds (hydrophobic) are better adsorbed than soluble compounds (hydrophilic). Therefore, polar compounds which tend to be hydrophilic are less well-adsorbed than non-polar compounds.

Natural organic acids such as humics are fairly well-adsorbed by GAC mesopores especially at low pHs. Humic substances are likely to be present in natural waters all year round, while industrial micro-pollutants, pesticides, taste and odor compounds and algal toxins are more sporadically present. NOM accounts for the majority of the GAC organic loading in drinking water facilities and greatly influence the length of time the GAC adsorber can be on line before regeneration is necessary. The surface charge of the GAC greatly affects adsorption of humic and fulvic acids (the major dissolved constituents of NOM) and other charged contaminants in water. The adsorption of these highly charged compounds will alter the adsptive properties of GAC for other compounds (Sontheimer et al., 1988 and Morris and Newcombe, 1993). Morris and Newcombe (1993) additionally found that the adsorption of humic matter from a raw source altered the surface properties of GAC. The adsorbed material caused the net charge of the GAC to be more negative.

Smaller pores are recognized as being most beneficial in adsorption because each wall of the pore exerts an attractive force, and in a small pore, adsorbed materials benefit from attractive forces from both walls in an overlapping manner (Moore et al., 2004). Therefore, it logically follows that smaller organic contaminants would easily fit into the micropores and be held in place by the overlapping attractive forces. This supports the conventional historical knowledge mentioned previously. Newcombe et al. (1998) demonstrated that NOM with nominal molecular weights below 3,000 mainly loaded into
micropores and somewhat less into mesopores, but that pore volume attributable to micropores and mesopores was lost almost equally through the adsorption cycle. This is likely due to the fact that new micropores are created as the mesopores partially fill with NOM (Newcombe et al., 1998).

GAC has been found effective in removing PPCPS and EDCs. Westerhoff, et al. (2005) found a correlation between log $K_{ow}$ (measure of hydrophobicity) and the removal of 22 pharmaceutical and personal care products by GAC. Kim, et al., (2007) found that GAC provided efficient removal (approximately 99%) of 14 pharmaceuticals, 6 hormones, 2 antibiotics and 3 personal care products. Snyder, et al., (2007) found that GAC was highly effective at removing 36 target chemicals in natural waters. However, breakthrough curves clearly demonstrated that compounds with greater hydrophilicity break through GAC more quickly than hydrophobic compounds. In full-scale applications, the impact of regeneration was observed as GAC filters that received frequent regeneration had minimal breakthrough of organic contaminants, while non-regenerated filters removed none of the target compounds. Yu et al., (2009) studied GAC for the removal of two pharmaceuticals (naproxen and carbamazepine) and one EDC (nonylphenol). The effect of NOM on adsorption capacity reduction was most pronounced for the acidic naproxen, followed by the neutral carbamazepine and with the least effect on the more hydrophobic nonylphenol. Kumar and Mohan (2011) studied fixed bed columns with a raw domestic sewage influent water spiked with EE2. The adsorption process demonstrated efficient removal of EE2 when used as a tertiary treatment unit. Yang, et al. (2011) researched advanced wastewater reclamation. In these studies, erythromycin and carbamazepine, which were resistant to biological
treatment, were eliminated by 74 to 88% by GAC. Primidone, DEET, and caffeine were not reduced by GAC adsorption. Kleywegt et al. (2011) used plant specific data to determine removal efficiency of the four most frequently detected compounds in Ontario drinking water systems at trace levels. The removal efficiency of carbamazepine was determined to be from 71 to 93% for drinking water systems using GAC. The observed removal efficiency of gemfibrozil was between 44 and 55% in drinking water systems using GAC. The use of GAC provided a removal efficiency improvement of BPA from 80 to 99%.

Because of the surface area created by pores, GAC provides an excellent substrate for biological activity. GAC pores provide protection from shear forces and the functional groups of the adsorbed organic material provides a mechanism for chemical binding (Carvalho, et al., 2001). Also, biofilms on a fixed media are less affected by organic loading changes than are suspended growth systems. Studies have shown that biologically active carbon can continue to be effective even when contaminant levels were low (Shi, et al., 1995).

This current research compared the effectiveness of GAC for removing trace organic contaminants to UV/H₂O₂ and determined whether GAC used before or after the process could reduce undesirable by-products. Different states of GAC exhaustion were explored. The effect of biologically active GAC was also considered. The effect of GAC pretreatment on UV/H₂O₂ electrical demand was also quantified.

2.2.4. Advanced Oxidation by UV/H₂O₂

UV/H₂O₂ is a promising technology for the destruction of EDCs, PPCPs and a broad-spectrum of synthetic organic contaminants and undesirable natural organic
constituents. UV/H$_2$O$_2$ was the major focus of this research. This technology combines the effects of direct and indirect UV photolysis (Pereira et al, 2007). The advantage of UV/H$_2$O$_2$ and other hydroxyl radical based advanced oxidation technologies compared to more commonly used oxidants is the high reactivity and non-selective nature of the radicals for oxidation independent of the nature and chemical bonding of the targeted compound.

Medium pressure (MP) and low pressure (LP) UV lamps are commonly used in drinking water treatment plants. MP lamps use more electrical energy, but require a smaller plant footprint. Both MP and LP lamps emit light at wavelengths that can cause hydroxyl radical formation in the presence of H$_2$O$_2$ and photolysis, however the difference in their spectrum (polychromatic versus monochromatic light respectively) may affect various chemical bonds differently, generating different degradation products. Figure 2.1 demonstrates the relative difference in MP and LP lamp emission at the same dose (Ijpelaar, et al., 2010). This work was performed as a pre-study to this present research.
Indirect UV photolysis with hydrogen peroxide ($\text{H}_2\text{O}_2$) results in the cleavage of the HO-OH bond, causing the formation of hydroxyl radicals (\cdot\text{OH}). Although the UV absorption coefficient of $\text{H}_2\text{O}_2$ is a function of UV wavelength, both LP and MP UV lamps emit wavelengths that can cause photolysis of $\text{H}_2\text{O}_2$ to generate hydroxyl radicals. UV photolysis of $\text{H}_2\text{O}_2$ is a rapid process and the produced hydroxyl radicals react non-selectively with organic compounds yielding carbon-centered radicals. They target mainly unsaturated bonds or abstract hydrogen from C-H bonds (Buxton, 1988) especially those in α-position to π-systems, amines, ethers, thioethers, and carbonyl compounds (Hovorka et al, 2001). These carbon-centered radicals in turn rapidly react with dissolved oxygen to form peroxyl-radicals, followed by the breakdown of peroxyl
radicals to form oxyl-radicals, and the breakdown of oxyl-radicals to other radicals and stable reaction intermediates (Hovorka et al., 2001). In UV/H$_2$O$_2$ systems many radical-based reactions take place (i.e., generation, propagation, termination). The efficiency of the process is dependent upon the rate of formation of hydroxyl radicals, the presence and concentrations of hydroxyl radical scavengers and other parameters (i.e., UV absorbance of the process water, type and concentration of other organic impurities in water such as natural organic matter, type and concentration of target organic contaminants, water temperature) (Antoniou et al., 2009). The most prominent scavengers are the dissolved organic compounds (DOC), and alkalinity (HCO$_3^-$, CO$_3^{2-}$), however, H$_2$O$_2$ will also react with hydroxyl radicals (Pereira et al., 2007).

The efficiency of the UV/H$_2$O$_2$ process is dependent upon the rate of formation of hydroxyl radicals, UV absorbance by the process water and the concentration of hydroxyl radical scavengers. UV absorption by the process water varies with the type and concentration of dissolved matter. NOM in drinking water sources is normally at least an order of magnitude greater in concentration than most target synthetic organic contaminants. NOM affects the efficiency of the UV/H$_2$O$_2$ process in two ways: as a hydroxyl radical scavenger and as an absorber of UV radiation. Like the target contaminants, NOM is attacked by hydroxyl radicals through fast and non-selective reactions. If UV radiation is absorbed, direct photolysis of contaminants is reduced and a lower amount of hydroxyl radicals is produced to accomplish advanced oxidation of contaminants.

The doses of UV and hydrogen peroxide required to achieve desired contaminant destruction depend on UV radiation absorbance and hydroxyl radical scavenging by
NOM. Drinking water sources differ in the type and amount of NOM present and some source waters have significant seasonal variations. Additionally, the UV/H\textsubscript{2}O\textsubscript{2} process can be inserted into a treatment plant at multiple points in the process resulting in differing NOM concentrations of influent to the UV/H\textsubscript{2}O\textsubscript{2} process. By understanding the effect of various concentrations and types of NOM on the UV/H\textsubscript{2}O\textsubscript{2} process, more efficient and cost effective installations can be designed. One of the largest costs of the UV/H\textsubscript{2}O\textsubscript{2} process is electrical energy, and energy consumption should be considered when designing the process. Thus, waters with high NOM concentrations generally require a greater capital investment and higher operating costs than low NOM waters to achieve like reductions in contaminants by UV/H\textsubscript{2}O\textsubscript{2}. A fundamental measurement of the energy efficiency of a UV advanced oxidation system is the Electrical Energy per Order (E\textsubscript{EO}). It is defined as “the number of kilowatt-hours of electrical energy required to reduce the concentration of a contaminant by one order of magnitude in a specified volume of water”, i.e., 1,000 L (Bolton et al., 2001, Sharpless et al., 2005). Both bench and pilot plant studies can be performed to assess the effect of NOM on process efficiency. Bench-scale collimated beam experiments can be used to understand better, how NOM affects UV/H\textsubscript{2}O\textsubscript{2} by providing a more controlled environment to test a range of degradation and UV doses. The formula used for the calculation of the E\textsubscript{EO} in this pilot study is:

\[
E\textsubscript{EO} = \frac{kWh}{m^3 \cdot \text{order}} = \frac{\text{UV reactor draw (kW)}}{\text{flow (m}^3/\text{h})} \times \log\left(\frac{C_{\text{inf}}}{C_{\text{eff}}}\right)
\]
The major thrust of this research was the study of UV/H$_2$O$_2$ destruction of contaminants, obtain a deeper understanding of problems caused by UV/H$_2$O$_2$ reactions with NOM and identify conditions and treatments that minimize the undesired by-products.

2.3. **Natural Organic Matter in Drinking Water**

NOM is present in drinking water sources in concentrations considerably greater than the synthetic organic contaminants (in the mg/L range). Concentration and composition of NOM varies with the source water. NOM is a problem to drinking water systems for several reasons. NOM interferes with coagulation, creates a disinfectant demand and produces assimilable organics that can populate the distribution system and harbor pathogens. NOM also organically loads granular activated carbon and interferes with target contaminant removal. NOM is the source of chlorinated and ozonated disinfection by-products. If a treatment technique requires oxidation or other chemical reaction, a major concern is the unintended consequence of those reactions on NOM.

Numerous methods have been established to assess the characteristics of NOM in drinking water. It is generally characterized relative to physical and chemical properties. Surrogates such as TOC and DOC and ultraviolet absorbance at 254 nm (UV$_{254}$) have been used to quantify NOM. Specific ultraviolet absorbance at 254 nm (SUVA) and UV spectroscopy has been used as a tool for understanding reactivity NOM (Reckhow, et al. 1990, Korshin et al., 1997, Weishaar 2003). Inorganic constituents of natural waters do not tend to absorb at wavelengths greater than 230 nm (Ogura and Hanya, 1966). As a result, absorbance in the 240 to 300 nm range gives an indication of NOM concentration. In NOM molecules, aromatic groups primarily associated with the humic and fulvic fractions of NOM absorb light in this range, (Christman et al., 1989). Korshin
et al., (1997) modeled the selective oxidation of NOM by chlorine by use of spectral analysis. He found that despite the overlapping of the LE, Bz and ET electron-transfer bands in NOM, they can be extracted from the UV spectra, even though their UV absorbance is centered at 180, 203 and 253 nm, respectively. However, only the Bz and ET bands were necessary to model the spectra in the 200 to 400 nm absorbance range, the range most indicative of NOM. The researchers found that oxidation by chlorination of NOM fractions with high concentrations of hydroxyl, carbonyl, ester and carboxyl-substituted aromatic rings caused the ET and Bz bands to contract and caused the ratio of ET absorbance to Bz absorbance to decrease. They used non-linear statistical regression software for data-fitting to “deconvolute” the bands in order to model. Much information about the concentration and nature of NOM can be gained from these relatively inexpensive methodologies.

More sophisticated characterization methods have also been employed. General characterization of NOM by polarity and acidity fractionation has been explored to understand NOM reactivity (Leenher et al., 2000, Croué, 2004). High performance size exclusion chromatography has been used to characterize NOM by molecular weight (Frimmel 1998). Huber, et al., 2011 has determined that a liquid chromatography system with organic carbon and organic nitrogen detectors can fractionate NOM into 1) biopolymers such as saccharides, peptides and proteins, 2) humic/fulvic acids, 3) hydrolysates of humic substances, 4) low molecular weight humic substances and 5) low molecular weight neutral compounds such as alcohols, aldehydes, ketones, etc. Fluorescence has been used to characterize NOM and most recently fluorescence excitation-emission matrices (F-EEM) coupled with various data analysis software has
been used to separate F-EEM data into protein and humic components (Stedmon, et al., 2003, Baghoth et al., 2011). Fractionation and pH adjustment of the water before F-EEM analysis has been used to separate the humic acid-like NOM from the fulvic acid-like NOM. In considering the reactivity of NOM during advanced oxidation, this distinction is important. Although, no perfect analytical methodologies have been established, it is important to understand how NOM affects the treatment process.

The reactivity of NOM with hydroxyl radicals has been related to the amount of quantified NOM as dissolved organic carbon (DOC) or the ultraviolet absorption (UVA) with a constant specific-UVA (SUVA, cm⁻¹ (mg/L)⁻¹) (Hoigne and Bader, 1979; Haag and Yao, 1993). However, NOM structure is not well defined and reaction rates with hydroxyl radicals vary. Westerhoff et al., (2007) determined by competition kinetics that the average second-order rate constants for reactions between NOM and the hydroxyl radical in multiple natural waters ranged from \(1.39 \times 10^8\) M⁻¹ s⁻¹ to \(4.53 \times 10^8\) M⁻¹ s⁻¹ for the reaction of hydroxyl radicals with NOM.

The quantity and nature of NOM and the effect of NOM on the efficiency of the process was considered in this current research. The kinetics of the NOM-hydroxyl radical reaction additionally were explored. Various tools were used to understand the effect of this reaction. A number of techniques were used to assess the changes to NOM as a result of treatment and the effect on water quality: TOC/DOC, SUVA, UV₂₅₄ absorbance, UV scans from (200-400 nm), AOC, including the Pseudomonas fluorescens strain P17 and Spirillum strain NOX components, direct measurement of biofilm production by annular reactor and trihalomethane and haloacetic acid formation potential. The electrical energy per order of contaminant reduction was calculated to obtain a
quantitative assessment of the energy required to destroy the contaminants at varying NOM conditions. An advanced oxidation model was used to better understand the kinetics of the NOM-hydroxyl radical reaction at three distinctly different NOM conditions.

2.3.1. Biofilm Potential Caused by UV/H\textsubscript{2}O\textsubscript{2}

The UV/H\textsubscript{2}O\textsubscript{2} process forms hydroxyl radicals that react non-selectively. Upon reaction with NOM, organic free radicals then can form small MW organic fractions such as aldehydes, ketones, alcohols, and carboxylic acids that can be used in microbial metabolism (Speitel et al., 1999). While the composition of NOM varies from location to location, there are some similarities in the structure. Humic substances comprise up to 75 percent of the NOM (Volk et al., 1997). Organic matter originating from soils is derived from plant matter, which has a high lignin content. Lignin has a predominant aromatic fraction. NOM also provides reduced carbon that supplies energy and carbon for bacterial metabolism (Kaplan et al., 2004). Kaplan and Gremm (1995) determined that 54% of the most biodegradable material in the waters sampled was humic in nature. Butterfield and colleagues (1997) additionally found that humic substances in the distribution system were the primary carbon source supporting distribution biofilm. However, while the formation of biofilm in the distribution system is believed to be ubiquitous, the degree of colonization varies from site to site.

As Weinrich et al., (2009) explained, biofilm production is a major cause of water quality issues in the distribution system, as human pathogens can reproduce and be protected from residual disinfectant. As was mentioned previously, biofilms can be responsible for
disinfectant depletion and can lead to problems with taste and odor. Nitrification can become a problem and corrosion rate can be increased.

Distribution system biofilm growth can be caused by several factors and is generally promoted through a combination of these factors. Temperature, assimilable organic carbon (AOC), availability of nutrients (trace inorganic compounds) and presence of residual disinfectant, all control microbial growth (Reasoner et al., 1991). LeChevallier et al., 1991 and 1996, investigated coliform regrowth in 31 drinking water systems. They found that there was a complex interaction of physical, chemical operational and engineering factors involved in bacterial regrowth. Temperature, particulate protection of microorganisms, types of organisms colonizing the distribution system (e.g., resistance of microbes to disinfection) and nutrient concentrations were all found to control the type and amount of biofilm (Baribeau et al., 2005). Kaplan et al. (2004) determined that the biodegradable organic carbon sources were vastly different in quantity and type in natural waters, and these differences in organic content influence the community of heterotrophic bacteria in biofilm.

Research to determine the exact chemical composition of biodegradable organic matter is on-going. It is known that lower molecular weight compounds are more easily transported across cell membranes enabling enzymatic reactions to proceed. Assimilable organic carbon (AOC) is often used to quantify regrowth potential and to gain insight into the types of compounds comprising biologically degradable carbon. The AOC method developed by van der Kooij et al. (1982 and 1984) makes use of two specific strains of organisms that allow for universal comparison of biofilm potential among diverse utilities. Pseudomonas fluorescens strain P17 is able to utilize various
compounds such as proteins, amino acids, carbohydrates, alcohols and aromatic acids, but does not grow well in carboxylic acids alone (LeChevallier et al., 1993). It has great nutritional variability. *Spirillum* strain NOX is more selective in its growth substrates. Only carboxylic acids and a few amino acids promote growth of NOX. In situations such as ozonation where compounds not utilized by P17 are present, *Spirillum* strain NOX is often used. Carboxylic acids promote more rapid growth of NOX than P17, thus NOX growth is a more sensitive indicator of the presence of these compounds. Also, in cases of low AOC, this organism tends to grow better than P17. Therefore, this method can be used to obtain information about the quantity and chemical composition of the assimilable materials (AwwaRF and KIWA, 1988). Van der Kooij (1992) has recommended that unchlorinated systems maintain AOC values below 10 µg/L. LeChevallier et al., (1990 and 1996) however, provided evidence that chlorinated systems may limit regrowth and coliform occurrence by maintaining AOC less than 50 to 100 µg/L.

Shi-hu et al., (2008) found that the AOC/TOC ratio increased with decreasing apparent molecular weight (MW). Hem and Efraimsen 2001 found 50-70% of the AOC fraction were <1000 Daltons molecular weight. Other researchers observed good correlation between apparent molecular weight distribution (AMWD) and UV absorbance (at 254 nm) to TOC ratio and biodegradability of raw waters (Goel et al., 1995). The AOC fraction is generally less than 1,000 MW, Hem and Efraimsen (2001), and can include sugars, fatty acids, amino acids and peptides (Haddix, et al, 2004). These results would confirm the simpler lower MW fractions would be the most assimilable by biodegrading microorganisms.
Wu (1991) studied the biodegradation of commercial humic acid after UV/H$_2$O$_2$ treatment. Wu was able to increase biodegradability by 17%. Biodegradable dissolved organic carbon (BDOC) increased from 0.1 to 1.3 mg/L in Lake Austin Water in continuous flow UV/H$_2$O$_2$ experiments and 0.52 to 0.87 mg/L in Lake Houston Water. Acetic and oxalic acids are often found as intermediates of the NOM oxidation process, and these acids biodegrade readily (Speitel et al., 1999). The creation of biodegradable compounds by UV/H$_2$O$_2$ treatment has also been reported by (Thomson et al., 2004, Toor and Mohseni 2007, Sarathy and Mohseni, 2009).

The pilot-scale systems that were used in this research include GAC columns to adsorb and potentially biodegrade intermediates and by-products. Organic biodegradation can be advantageous in drinking water treatment, and can be accomplished through biologically active GAC. But, biodegradable organics leaving the plant can cause microbial regrowth in the distribution system, a potentially serious problem. This current research explores the increase of biofilm potential by the UV/H$_2$O$_2$ process, examines under which conditions it becomes most problematic and suggests mitigation strategies.

### 2.3.2. DBP Formation Potential Caused by UV/H$_2$O$_2$

Free chlorine is a commonly used disinfectant in North America and other parts of the world. Since the 1970s it has been known that disinfection by-products with potential health effects were formed in chlorinated drinking water. Many researchers have explored chlorination reaction pathways leading to THM and other disinfection by-product formation (Christman et al., 1978; Norwood et al., 1980; Reckhow and Singer, 1985; Rook, 1974, 1977). Aquatic natural organic matter (NOM) is complex and all reaction mechanisms between NOM and chlorine have not been elucidated. Rook
(1977) theorized that humic and fulvic acids have hydroxylated aromatic rings with two free meta-positioned OH groups, available active sites for trihalomethane formation, but the mechanisms were not been well-defined. Researchers have different opinions about which fractions of NOM are the predominant precursors of THMs and HAAs. Some researchers report that hydrophilic/polar NOM is more prevalent in the formation of HAAs than THMs (Hwang et al., 2001), whereas others implicate hydrophobic/non-polar NOM (Liang and Singer, 2003).

NOM is generally characterized as hydrophobic, transphilic, hydrophilic with acid, base and neutral subdivisions (Croué et al., 2006). These operationally defined fractions can provide information relative to DBP precursors. Researchers have determined that the hydrophobic/non-polar NOM accounts for the majority of DBP formation (Liang and Singer, 2003). However, Hwang et al. (2001) found that even though upon chlorination non-polar NOM generally results in more DBPs on an organic carbon basis, polar NOM can produce a significant amount of DBPs, particularly haloacetic acids. Activated aromatic species such as β-dicarbonyl compounds have also been identified as reactive DBP precursors (Dickenson, et al., 2008).

The United States Environmental Protection Agency (USEPA) promulgated the Disinfectants/Disinfection By-product Rule (USEPA, 2006) setting maximum contaminant levels (MCLs) for the sum of four trihalomethanes (THM) and the sum of five haloacetic acids (HAA5) at 0.080 mg/L and 0.060 mg/L, respectively. This Rule required compliance to be determined on an annual running average of multiple locations. The Stage II Rule that became effective in 2012 requires that each sampling location complies with the MCLs listed above on an annual running average. In 2005
the World Health Organization set acute guidelines for the individual THMs emphasizing the varying toxicity of these compounds. The guideline for chloroform was set at 300 µg/L, bromodichloromethane at 60 µg/L, dibromochloromethane at 200 µg/L and bromoform at 100 µg/L.

Over the past 15 years several studies have suggested a modest epidemiological association between regulated THMs in drinking water and negative reproductive results, including spontaneous abortion, neural tube defects and intrauterine growth retardation (Bove et al., 1995; Waller et al., 1998; Klotz et al., 1999). Associations with bromodichloromethane were suggested at levels less than 20 µg/L (Dodds and King 2001). However, one very robust study conducted by drinking water experts and epidemiologists, Savitz and colleagues (2005), does not show a significant association in spontaneous abortions related to DBP concentrations.

Although many researchers have reported that at disinfection doses UV does not increase DBP formation, Magnuson et al., (2002) found that UV direct photolysis and UV/H₂O₂ can alter extracted NOM, increasing disinfection by-product precursors. Mass spectra varied with UV dose ranging from 20 to 140 mJ/cm², indicating a change in NOM chemical structure. The change in dose also appeared to increase the reactivity of the extracted organic matter with subsequent chlorination. The magnitude of spectral changes was greater for medium pressure than low pressure lamps at equal doses.

Some researchers have studied the reduction of NOM and DBP precursors through UV/H₂O₂. Matilainen and Sillanpää (2010) and Bond, et al. (2011) have published comprehensive review articles that summarize this NOM and DBP formation potential work, respectively. Some researchers have found that at lower more practical UV/H₂O₂
conditions small increases in DBP formation potential can occur (Kleiser and Frimmel, 2000, Toor and Moseni, 2007, Dotson et al., (2010) and Sarathy and Mohseni, 2010). Kleiser and Frimmel (2000) found that with short irradiation times, the UV/H₂O₂ process increased THM precursors. Toor and Mohseni (2007) observed that UV/H₂O₂ was effective in reducing DBP formation potential only at UV doses >1000 mJ/cm² and at H₂O₂ doses > 23 mg/L. Sarathy and Mosheni (2010) reported that at UV doses between 500 and 2000 mJ/cm² with 15 mg/L of H₂O₂, there was a significant reduction in TOC and SUVA that was not matched by the small reductions in DBP precursors. However, when hydrophobic humic acids were reduced, improved reductions were noted. Dotson and colleagues (2010) reported that at a UV dose of 1000 mJ/cm² and 10 mg/L H₂O₂ THM yield was increased. The researchers found that THM yield correlated with hydroxyl radical exposure.

In this current research, various water temperatures and water quality conditions were assessed to determine the full effect of UV/H₂O₂ on disinfection by-product formation. GAC use before and after the UV/H₂O₂ process was evaluated for disinfection by-product potential reduction. The best way to assess the potential of disinfection by-product formation is to develop a simulated distribution system protocol that mimics the water quality conditions of the distribution system. This protocol was developed used for each process influent and effluent water scenario, so that the effects of each treatment process and their interaction could be evaluated.
2.4. References


Water Chlorination: Chemistry, Environmental Impact and Health Effects, 5:1229-1257 Lewis, Chelsea, MI.


Sontheimer, H., Crittenden, J.C., Summers, R.S. (1988) Activated Carbon for Water Treatment. 2nd ed., DVGW-Forschungsstelle, University of Karlsruhe, Germany, distributed in the USA by AWWA.


Chapter 3

Natural Organic Matter: Effect on Contaminant Destruction by UV/H$_2$O$_2$
Advanced oxidation with ultraviolet light and hydrogen peroxide (UV/H$_2$O$_2$) produces hydroxyl radicals that have the potential to degrade a wide-range of organic micro-pollutants in water. However, natural organic matter can interfere with target contaminant destruction. This study evaluated the effect of natural organic matter on contaminant destruction by UV/H$_2$O$_2$. Seven contaminants were evaluated by low-pressure UV pilot-scale experiments. UV scans collected before and after the reactors demonstrated the change in NOM due to hydroxyl attack. Methyl tert-butyl ether (MTBE) destruction by UV/H$_2$O$_2$ was evaluated using a bench-top collimated beam unit. To reflect different amounts and types of natural organic matter in drinking water; conventionally treated (CONV) water, GAC treated (Post-GAC) water from a drinking water treatment plant and laboratory generated reverse osmosis (RO) water were examined. Water with higher natural organic matter concentration (NOM) and humic content, required higher UV fluence (dose) and energy than water with lower NOM to achieve comparable results. Higher NOM resulted in a higher electrical energy per order (E$_{EO}$) requirement for UV/H$_2$O$_2$ target contaminant destruction. Higher NOM increased the E$_{EO}$ similarly for the seven compounds considered: atrazine, metolachlor, MTBE, methylisoborneol (MIB), ibuprofen, gemfibrozil, and 17α-ethynylestradiol (EE2). MTBE destruction correlated very well with the SUVA values. The E$_{EO}$ for MTBE destruction correlated well with SUVA for both the pilot-scale and bench-scale experiments.
3. Natural Organic Matter: Effect on Contaminant Destruction by UV/H$_2$O$_2$

3.1. Introduction

Not only are water utilities facing concerns from traditionally troublesome natural organic contaminants such as methylisoborneol and geosmin and regionally problematic occurrences of synthetic organic contaminants such as methyl tert-butyl ether (MTBE), but more recently trace contaminants of pharmaceutical and personal care products (PPCP) have been reported in technical and popular publications. However, these findings are not new. In the 1930s and 1940s scientists first noted that some synthetic compounds could mimic natural endocrine hormones in animals. These chemicals were identified as endocrine disruptors (EDCs) and included a variety of compounds, which could block the natural estrogen, testosterone and thyroidal hormones in animals, resulting reproductive problems in many aquatic wildlife species. (Walker and Janney, 1930; Stroud, 1940). In the middle of the twentieth century dichlorodiphenyl trichloroethane (DDT) was shown to be an endocrine disrupting chemical (Bitman et al., 1968) and later found to exhibit teratogenic effects (Guillette, et al., 1994). Researchers have investigated EDCs in the US waters since the 1960s (Stumm-Zollinger, 1965; Tabak and Bunch, 1970), and estrogenic impacts of wastewater containing EDCs have been observed (Routledge et al., 1998). Examples of EDCs with well-documented endocrine disruptive activity are DDT, atrazine, and 17 $\alpha$- ethynyl estradiol (EE2), while broader groups include steroid hormones, alkylphenols, phthalates and phytoestrogens (Snyder et al., 2008). Another group of environmental contaminants, which cause customer concern and may have human health effects, is the pharmaceuticals and personal care products (PPCPs). This category includes a
variety of compounds such as antibiotics, antiseptics, medical contrast material, surfactants, heart medications and analgesics. They enter the environment through wastewater discharges, animal operations, agricultural runoff and groundwater contamination through solid waste disposal. The range of concentrations of these micro-pollutants in U.S. waters varies between non-detectable and up to 20 µg/L (atrazine) with most contaminant concentrations being in the ng/L range (Snyder et al., 2007). A number of studies have found trace detections of these compounds in finished drinking water. Stackelberg et al. (2004), found 17 PPCPs in finished water systems. Phthalate esters have also been reported in finished water (Luks-Betlej et al., 2001; Psillikis, et al., 2003). Herberer (2001) found clofibric acid, propylphenazone and diclofenac in finished drinking water. While the concentrations are generally well-below therapeutic values, the synergistic effects, and the effects of lifetime exposures are unknown.

The application of the ultraviolet light and hydrogen peroxide (UV/H₂O₂) advanced oxidation process to drinking water produces energy and hydroxyl radicals that have the potential to degrade a wide-range of organic micro-pollutants. However, natural organic matter (NOM) interferes with target contaminant destruction (He, et al., 2012). The efficiency of the UV/H₂O₂ process is dependent upon the rate of formation of hydroxyl radicals, UV absorbance by the process water, and the concentration of hydroxyl radical scavengers and the reactivity of the target compounds. UV absorption by the process water varies with the type and concentration of dissolved matter. NOM in drinking water sources is normally at least an order of magnitude greater in concentration than most target synthetic organic contaminants. NOM affects the efficiency of the UV/H₂O₂ process in two ways: as a hydroxyl radical scavenger and as an absorber of UV
radiation. Like the target contaminants, NOM is attacked by hydroxyl radicals through fast and non-selective reactions. If UV radiation is absorbed by NOM, direct photolysis of contaminants is reduced and less hydroxyl radicals are produced to accomplish advanced oxidation of contaminants. The reactivity of NOM with hydroxyl radicals has been related to the amount of quantified NOM as dissolved organic carbon (DOC) or the ultraviolet absorption with a constant specific-ultraviolet absorption 254 nm (SUVA) (Hoigne and Bader, 1979; Haag and Yao, 1993). However, NOM structure is not well defined and reaction rates with hydroxyl radicals vary. Westerhoff et al., (2007) determined by competition kinetics that the average second-order rate constants for reactions between NOM and the hydroxyl radical in multiple natural waters ranged from $1.39 \times 10^8 \text{M}^{-1} \text{s}^{-1}$ to $4.53 \times 10^8 \text{M}^{-1} \text{s}^{-1}$.

Various methods have been established to assess the characteristics of NOM in drinking water. It is generally characterized relative to physical and chemical properties. Surrogates such as total organic carbon (TOC) and dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UV$_{254}$) have been used to quantify NOM. SUVA and UV spectroscopy has been used as a tool for understanding the reactivity of NOM (Reckhow, et al. 1990; Korshin et al., 1997; Weishaar 2003). Inorganic constituents of natural waters do not tend to absorb at wavelengths greater than 230 nm (Ogura and Hanya, 1966). As a result, absorbance in the 240 to 300 nm range gives an indication of NOM concentration. In NOM molecules aromatic groups primarily associated with the humic and fulvic fractions of NOM absorb light in this range, (Christman et al., 1989). Korshin et al., (1997) modeled the selective oxidation of NOM by chlorine by using spectral analysis. He found that despite the overlapping of the LE, Bz and ET electron-
transfer bands in NOM, they can be extracted from the UV spectra, even though their UV absorbance is centered at 180, 203 and 253 nm, respectively. However, only the Bz and ET bands were necessary to model the spectra in the 200 to 400 nm absorbance range, the range most indicative of NOM. Korshin and colleagues found that oxidation by chlorination of NOM fractions with high concentrations of hydroxyl, carbonyl, ester and carboxyl-substituted aromatic rings caused the ET and Bz bands to contract and caused the ratio of ET absorbance to Bz absorbance to decrease. They used non-linear statistical regression software for data-fitting to “deconvolute” the bands in order to model. UV scans in these wavelengths can be used as a practical tool to gain some understanding of NOM and its changes.

In full-scale facilities, the doses of UV and hydrogen peroxide required to achieve desired contaminant destruction in part depend on UV radiation absorbance and hydroxyl radical scavenging by NOM. Drinking water sources differ in the type and amount of NOM present and some source waters have significant seasonal variations. The UV/H$_2$O$_2$ process can be inserted into a treatment plant at multiple points in the treatment process resulting in differing NOM concentrations of influent to the UV/H$_2$O$_2$ process. By understanding the effect of various concentrations and types of NOM on the UV/H$_2$O$_2$ process, more efficient and cost effective installations can be designed. One of the largest costs of the UV/H$_2$O$_2$ process is electrical energy, and energy consumption should be considered when designing the process. Thus, waters with high NOM concentrations generally require a greater capital investment and higher operating costs than low NOM waters to achieve like reductions in contaminants by UV/H$_2$O$_2$. A fundamental measurement of the energy efficiency of an advanced oxidation system is
the Electrical Energy per Order ($E_{EO}$). It is defined as “the number of kilowatt-hours of electrical energy required to reduce the concentration of a contaminant by one order of magnitude in a specified volume of water”, i.e., 1,000 L (Bolton et al., 2001; Sharpless et al., 2005). Although both bench and pilot plant studies can be performed to assess the effect of NOM on process efficiency, pilot-scale experiments are typically used. Bench-scale collimated beam experiments can be used to better understand, how NOM affects UV/H$_2$O$_2$ process efficiency by providing a more controlled environment to test a range of reaction conditions and UV doses.

A 12-month UV/H$_2$O$_2$ pilot study and a 16-month bench-scale study were performed at Greater Cincinnati Water Work’s (GCWW) Richard Miller Treatment Plant (RMTP) to quantify the destruction of organic micro-pollutants by UV/H$_2$O$_2$ under varying natural organic matter (NOM) conditions and to evaluate NOM’s effect on energy consumption. A bench-scale evaluation of NOM’s impact on MTBE destruction followed to determine NOM’s correlation with organic parameters and the reaction rates for NOM in these waters. This study was unique because it considered a variety of NOM concentrations with a range of contaminants, examining both practical and fundamental aspects of NOM’s role in UV/H$_2$O$_2$ treatment. The study made use of waters with seasonal water quality variations and waters exiting granular activated carbon (GAC) at differing states of exhaustion. Realistic targets for contaminant destruction were chosen and the percent destruction held constant throughout the pilot-scale work. This research combined the practicality of real world conditions at a drinking water treatment plant with laboratory controlled findings.
3.2. Materials, Methods and Facilities

The source water for the UV/H\textsubscript{2}O\textsubscript{2} pilot influent and collimated beam studies was drawn from two locations within Greater Cincinnati Water Works’ (GCWW) Ohio River water treatment plant. (See Figure 3.1.) Location 1 was after coagulation, settling and filtration, i.e., conventional treatment (CONV). Location 2 was from combined GAC adsorber effluent (Post-GAC). During the pilot-scale phase, the treatment plant drew water from the Ohio River (TOC ranging from 1.9 to 4.0 mg/L, averaging 2.5 mg/L). An average of 12.7 mg/L alum and 1.2 mg/L cationic polymer was added to the water prior to primary settling. The water was then flocculated and settled in lamella plate-pack settlers with a design detention time of 36 minutes. This process removed approximately 20 to 25% of the TOC. The water then passed through two settling and storage reservoirs with a two to five day detention (residence time). Iron sulfate (averaging 1.3 mg/L) was added intermittently to the settled water before secondary sedimentation. The water was then filtered through rapid sand filters containing 61 – 76.2 cm (24 - 30 in) of sand at a rate of 7.3 m/hr (3.0 gpm/ft\textsuperscript{2}). This filtered water was used as one of the two pilot influent process streams (CONV process stream). At this point the TOC concentration had been decreased by 30% on average (from 2.5 to 1.8 mg/L), and SUVA from 3.4 to 2.6 L/mg-m on average.

Water exiting the filters was sent to the GAC facility. The GAC contactors were filled with 11.4 ft (3.5 m) of carbon and were operated in a down-flow, gravity mode. Carbon contact time averaged about 15-20 minutes during the study. The GAC removed a broad spectrum of organic compounds present in the Ohio River. Water entering the GAC facility had a TOC averaging 1.86 mg/L; water exiting the facility had a TOC
averaging 0.89 mg/L. The GAC facility also served to reduce significantly disinfection by-product (DBP) precursors and biodegradable organic carbon. After becoming exhausted (average combined effluent of 150 days, maximum combined effluent 200 days), the GAC was thermally reactivated onsite. Virgin make-up GAC was added to achieve the 3.5 m (11.4 ft) GAC bed.

This carbon treated water was used as the second of the two pilot influent process streams (Post-GAC process stream). After GAC adsorption, the TOC concentration was reduced by 65% (from 2.5 to 0.85 mg/L) of the raw water concentration and SUVA was reduced from 3.4 to 1.7 L/mg-m. The Post-GAC water was lower in TOC and generally followed the seasonal trend of the CONV water.

**Figure 3.1:** Schematic of the Richard Miller Treatment Plant

The pilot unit was in continuous operation from October of 2007 until October 2008. It consisted of a constant head tank, the peroxide and contaminant feed systems, and the UV reactors. CONV or Post GAC water was pumped to a constant head tank. The contaminant solutions and the 8% hydrogen peroxide solution (to achieve a dose of 10 mg/L) were injected through two inline injection mixers. The LP reactor (Aquionics
The reactor included an immersed pre-calibrated UV monitor (Hanovia) sensitive to UVC wavelengths, and a manual rubber wiper. A digital display on the power supply box indicated the UV intensity, UV dose, run hours, and temperature, and allowed for flow and UVT<sub>254</sub> input for the computation of the UV dose. The flow range through the reactors could vary between 1.8 to 10 m<sup>3</sup>/hr (8 to 44 gpm) (Metz et al., 2011a and b). (See Figure 3.2.) Pilot plant UV doses were set to achieve a constant 80% reduction of atrazine that reduced pharmaceutical compounds, pesticides and odor producing compounds by more than ninety percent and MTBE 50 to 60%.

The effluent from both UV reactors and the control water (pilot influent water before the hydrogen peroxide injection point but after the contaminant injection point) were pumped to four GAC pilot columns. Two GAC columns were fed by the control water, control columns 1 and 2. Each of the remaining two columns received the effluent of the LP reactor or the effluent of the MP reactor. The GAC columns contained reactivated GAC acquired directly from the reactivation facility at Richard Miller Treatment Plant (RMTP) Cincinnati, Ohio. The GAC was bituminous coal, US mesh size 12x40 with 0.55-0.75mm effective size, and apparent density of 0.48 g/cm<sup>3</sup> (30 lbs/ft<sup>3</sup>). The GAC
bed depth in the 10.2 cm (4 inch) diameter columns was about 173 cm (68 inches), yielding an empty bed contact time of 15 minutes.

Figure 3.2: Schematic of the UV/H$_2$O$_2$ Pilot Plant

Many contaminants were considered for inclusion in this study to represent a diversity of compounds, so the factors for selection were:

- Representation of major emerging contaminant groups
- Chemical formulas, bonds and structure of the compounds
- Solubility and second order reaction rate constant with the hydroxyl radical
- Frequency of occurrence and concentration in source water

The contaminants selected for spiking were atrazine, metolachlor, MTBE, methylisoborneol (MIB), ibuprofen, gemfibrozil, and 17α-ethynylestradiol. Their
structures and constants related to advanced oxidation and solubility are shown in Table 3.1. The constant $k_{OH}$ is the second order reaction rate constant between the compound and hydroxyl radicals, while $K_{ow}$ is the octanol-water partition coefficient.
Table 3.1: Selected contaminants for pilot spiking at GCWW

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Major Groups</th>
<th>( k_{OH} ) (M(^{-1})s(^{-1}))</th>
<th>( \log K_{ow} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td><img src="image" alt="Atrazine Structure" /></td>
<td>Triazine ring, secondary amines</td>
<td>(2.6 \times 10^9)</td>
<td>2.61</td>
</tr>
<tr>
<td>Metolachlor</td>
<td><img src="image" alt="Metolachlor Structure" /></td>
<td>Aromatic ring, amide, methoxy, chlorine</td>
<td>(6.9 \times 10^9)</td>
<td>3.13</td>
</tr>
<tr>
<td>MTBE</td>
<td><img src="image" alt="MTBE Structure" /></td>
<td>Ether</td>
<td>(1.6 \times 10^9)</td>
<td>1.20</td>
</tr>
<tr>
<td>MIB</td>
<td><img src="image" alt="MIB Structure" /></td>
<td>Alcohol</td>
<td>(8.2 \times 10^9)</td>
<td>3.1</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td><img src="image" alt="Ibuprofen Structure" /></td>
<td>Aromatic ring, carboxylic acid</td>
<td>(7.4 \times 10^9)</td>
<td>3.97</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td><img src="image" alt="Gemfibrozil Structure" /></td>
<td>Aromatic ring, carboxylic acid, ether</td>
<td>(10 \times 10^9)</td>
<td>4.77</td>
</tr>
<tr>
<td>17 α-ethynylestradiol (EE2)</td>
<td><img src="image" alt="EE2 Structure" /></td>
<td>Phenol, ethynyl, aliphatic rings, alcohol</td>
<td>(1.08 \times 10^{10})</td>
<td>3.67</td>
</tr>
</tbody>
</table>

(1) Haag and Yao, 1992  
(2) Haag and Yao, 1992  
(3) Changlong et al., 2007  
(4) Changlong et al., 2007  
(5) Kavanaugh et al., 2003  
(6) Kavanaugh et al., 2003  
(7) Glaze et al., 1987  
(8) Westerhoff et al., 2005  
(9) Razavi et al., 2009  
(10) Razavi et al., 2009  
(11) Razavi et al., 2009  
(12) Rosenfeldt and Linden, 2004  
(13) Rosenfeldt and Linden, 2004  
(14) SCR Environmental Science Database, 2007
The contaminants were purchased in pure form with the exception of MIB, which was purchased dissolved in laboratory pure water. The contaminant stock solution was made by initially hydrating the powdered contaminants with laboratory pure water, then adding metolachlor and MTBE, followed by a 24 hour mixing period in the dark. The solution was then vacuum-filtered using 0.45 µm membrane, and lastly the MIB solution was added and mixed into the stock solution. The stock solutions were prepared immediately before the spiking events to avoid degradation of the contaminants. The contaminants were spiked to achieve pilot influent concentrations ranging from 40 ng/L to 10 µg/L, depending on the contaminant. Table 3.2 presents the spiked concentration of each contaminant.
Table 3.2: Origin and spiking level of contaminants at GCWW’s pilot unit.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Manufacturer</th>
<th>Purchased form</th>
<th>Spiking level</th>
<th>Analytical method</th>
<th>Method Detection Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>Supelco</td>
<td>Powder 98% pure</td>
<td>2 µg/L</td>
<td>USEPA 525.2</td>
<td>0.1 µg/L</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>Supelco</td>
<td>Liquid 99.5% pure</td>
<td>2 µg/L</td>
<td>USEPA 525.2</td>
<td>0.1 µg/L</td>
</tr>
<tr>
<td>MTBE</td>
<td>Supelco</td>
<td>1000mg ampule</td>
<td>4 µg/L</td>
<td>USEPA 524.2</td>
<td>0.2 µg/L</td>
</tr>
<tr>
<td>MIB</td>
<td>Arizona State University</td>
<td>DI Solution 40mg/L</td>
<td>40 ng/L</td>
<td>AWWA 6040D</td>
<td>2 ng/L</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>Sigma Aldrich</td>
<td>Powder 98% pure</td>
<td>10 µg/L</td>
<td>KWR LOA-602</td>
<td>0.5 µg/L</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>Sigma Aldrich</td>
<td>Powder 99% pure</td>
<td>2 µg/L</td>
<td>KWR LOA-602</td>
<td>0.1 µg/L</td>
</tr>
<tr>
<td>EE2</td>
<td>Sigma Aldrich</td>
<td>Powder 98% pure</td>
<td>100 ng/L</td>
<td>KWR LOA-539</td>
<td>5 ng/L</td>
</tr>
</tbody>
</table>

The contaminant samples were collected in triplicates in glass and polypropylene bottles and vials using 0.4 g sodium sulfite to quench the residual hydrogen peroxide. Atrazine, metolachlor, MTBE and MIB were analyzed at the RMTP plant, while the samples with ibuprofen, gemfibrozil, and 17-α-ethynylestradiol were frozen and sent to KWR Watercycle Research Institute (KWR) in the Netherlands for analyses. Information on the specific analytical methods can be found in Table 3.2. All other water quality parameters were analyzed by methods from *Standard Methods for the Examination of*
Water and Wastewater (APHS et al., 2005). It should be noted that breakdown products were not considered and the effectiveness of the process was determined by the disappearance of the parent compound. Because all of the waters were filtered, no difference was observed between TOC and dissolved organic carbon (DOC); therefore, TOC was consistently used through the study.

The collimated beam studies were conducted using a low-pressure, bench-scale collimated beam unit. This batch unit was designed to irradiate liquid samples in a controlled manner. The top of the unit housed four low-pressure, mercury, ultraviolet (germicidal) lamps (15W). UV light exposure was controlled by a shutter and an open Petri dish sits upon a stir plate that was 30 cm away from the lamps. The UV dose was controlled by the length of time the batch sample was irradiated. In the case of the collimated beam unit “fluence” is a somewhat better technical term than “dose”, but “dose” will be used in this paper for consistency. Irradiation time and UV dose were calculated by accounting for a variety of factors including radiometer readings, surface reflection, sample depth, UV transmittance, and Petri factor based on work by Bolton and Linden (2003). To reflect different amounts and types of natural organic matter in the drinking water, conventionally treated (CONV) water, GAC treated (Post-GAC) water and laboratory generated reverse osmosis (RO) water were used as test waters. The study was performed over 16 months, which allowed seasonal variation in the water to be examined. Also, the effluent from individual GAC contactors was collected throughout the period to reflect diverse TOC and SUVA values. MTBE was spiked into the source waters at a concentration of 4 µg/L.
After determining irradiation times for desired UV doses, a 100 mL batch sample of MTBE-spiked source water was placed in the collimated beam unit with the shutter closed. Ten mg/L hydrogen peroxide was added to the Petri dish and after mixing for 10 seconds, the shutter was pulled and the sample was irradiated for the pre-determined amount of time. At the end of every experiment, a simulated blank sample was held in the collimated beam unit for the time needed for the highest UV dose. This sample contained the initial target MTBE concentration, but the shutter remained closed, so that the sample was not irradiated. This simulation was performed to be certain that there was no volatilization of MTBE.

The samples for elemental analysis were concentrated and dried by USEPA employees and contractors at the GCWW Ohio River plant. The water was treated and concentrated by ultrafiltration, ion exchange and reverse osmosis (Pressman et al., 2010). Over five days, approximately 3000 L of water was concentrated 150 x 200 times. Two-stage barium chloride treatment was used to precipitate sulfate and the concentrate was lyophilized in a freeze-drying chamber with a VirTual EL control system (McCurry et al., 2012). The elemental analysis was performed by Huffman laboratory, Golden Colorado.

The formula used for the calculation of the $E_{EO}$ for flow through units is:

$$E_{EO} = \frac{\text{kWh}}{m^3 \cdot \text{order}} = \frac{\text{UV reactor draw (kW)}}{\text{flow (m}^3/\text{h})} \times \log \left( \frac{C_{\text{ref}}}{C_{\text{eff}}} \right)$$

This calculation can be used to determine the impact of water quality on process efficiency and cost. The formula used for the calculation of the $E_{EO}$ for batch units is
similar, except that time of the batch run in hours (h) is multiplied by the power term in
the numerator and volume (m$^3$) is substituted for flow in the denominator (Bolton et al.,
2001).

3.3. Results and Discussion

Table 3.3 presents pertinent water quality data for the two plant sampling locations. The
CONV pilot influent stream was more variable in water quality than the Post-GAC pilot
influent stream. From this data, it is obvious that the Post-GAC water has considerably
less organic content than the CONV water. SUVA is a measure of aromaticity and
conjugated double bonds and therefore an indicator of humic content. SUVA was much
lower in the Post-GAC water 2.6 L/mg-m on average for CONV water vs. 1.7 L/mg-m on
average for Post-GAC water. Not only was the organic material lower in concentration,
but it was also of a different character, i.e., lower molecular weight NOM. GAC is known
to preferentially remove the higher molecular weight NOM such as humic acids and
hydrophobic compounds. Note that alkalinity and anion concentration did not change
through the GAC adsorption process. In addition to CONV and Post-GAC water,
aboratory treated reverse osmosis (RO) water was used in the collimated beam testing.
The RO water, obviously, contained very little organic material. TOC averaged 0.033
mg/L, SUVA 0.45 L/mg-m, alkalinity 3.2 mg/L and pH 6.7.
Table 3.3: Water quality of CONV and Post-GAC water at RMTP – pilot plant influent and collimated beam study water

<table>
<thead>
<tr>
<th>Water Quality Parameter</th>
<th>CONV</th>
<th></th>
<th></th>
<th>Post-GAC</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Minimum</td>
<td>Maximum</td>
<td>Average</td>
<td>Minimum</td>
<td>Maximum</td>
</tr>
<tr>
<td>pH</td>
<td>7.8</td>
<td>7.2</td>
<td>8.2</td>
<td>7.7</td>
<td>7.3</td>
<td>8.3</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>1.8</td>
<td>1.2</td>
<td>2.6</td>
<td>0.85</td>
<td>0.4</td>
<td>1.4</td>
</tr>
<tr>
<td>UV$_{254}$ (cm$^{-1}$)</td>
<td>0.046</td>
<td>0.024</td>
<td>0.086</td>
<td>0.013</td>
<td>0.002</td>
<td>0.024</td>
</tr>
<tr>
<td>Total Alkalinity (mg/L as CaCO$_3$)</td>
<td>65</td>
<td>48</td>
<td>82</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature ºC</td>
<td>16</td>
<td>4.5</td>
<td>28</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

GAC adsorption was very effective in removing spiked contaminants, and provided an impenetrable barrier when preceded by UV/H$_2$O$_2$. Each of the seven compounds spiked into the process were removed to below the detection levels (See Table 3.2.) in the GAC effluent streams when the GAC influent stream was pretreated with UV/H$_2$O$_2$. GAC without UV/H$_2$O$_2$ pretreatment removed six of the seven compounds to below detectible concentrations for all four quarters. MTBE was the only compound detected in the fourth quarter of GAC run (day 286). MTBE was detected at a concentration of 0.31 and 0.26 µg/L, respectively in control columns 1 and 2. It should be noted that these detections represent a 94 to 95% removal, which was significantly better than the 54 to 56% removal achieved by UV/H$_2$O$_2$ alone. These results agree with the results of Kim, et al., (2007) and Kleywegt et al. (2011). Table 3.1 presents the partition coefficients ($K_{OW}$ values) that confirm that MTBE has the lowest log $K_{OW}$ and highest
solubility in water and was therefore expected to be the least adsorbed of the contaminants tested (Westerhoff et al., 2005).

The electrical energy per order $E_{EO}$ for the degradation of each contaminant during the pilot study was calculated based on the energy rating of the reactor’s lamps, the flow through the reactor and the influent and effluent concentration of the contaminant. The $E_{EO}$ values of the contaminants processed through the LP reactor are shown in Figures 3.3A and 3.3B for the CONV and Post-GAC water. The $E_{EO}$ values of the CONV water influent were higher than the values required for Post-GAC water influent. (See Table 3.4A.) The higher UV$_{254}$ absorbance values and TOC concentrations of the CONV water compared to the Post-GAC water explained this difference. 17-$\alpha$-ethynylestradiol, metolachlor and gemfibrozil had the lowest $E_{EO}$ with average values ranging from 0.17 to 0.20 kWh/m$^3$-order for CONV influent and 0.10 kWh/m$^3$-order for Post-GAC influent. MIB had the next lowest average $E_{EO}$ values, 0.20 kWh/m$^3$-order for CONV influent and 0.12 kWh/m$^3$-order for Post-GAC influent. Atrazine and ibuprofen followed with average $E_{EO}$ values of 0.30 and 0.27 kWh/m$^3$-order, respectively for CONV influent and 0.18 and 0.17 kWh/m$^3$-order, respectively for Post-GAC influent. MTBE had the highest energy requirements, 0.48 kWh/m$^3$-order for the CONV influent and 0.31 kWh/m$^3$-order for the Post-GAC influent. This ranking of $E_{EO}$ values agreed well with the reaction rate constants of hydroxyl radicals ($k_{OH}$) for these contaminants. (See Table 3.1.) MTBE had the lowest reported reaction rate at $1.6 \times 10^9$ M$^{-1}$s$^{-1}$ (Kavanaugh et al., 2003) and 17-$\alpha$-ethynylestradiol had the highest reported reaction rate of $1.08 \times 10^{10}$ M$^{-1}$s$^{-1}$ (Rosenfeldt and Linden, 2004). Therefore, it would be expected that 17-$\alpha$-ethynylestradiol would have the lowest average $E_{EO}$ value and MTBE would have the highest energy requirements.
requirement among the other contaminants. The $E_{EO}$ ratios between the CONV and Post-GAC water range between 1.5 and 2.0 for all contaminants. (See Table 3.4A.) These ratios would indicate that NOM had a similar scavenging effect on the destruction of all the compounds.

Figures 3.3C and 3.3D show the calculated $E_{EO}$ values for the MP reactor for UV/H$_2$O$_2$ with CONV (Figure 3.3C) and Post-GAC (Figure 3.3D) pilot influent water. Overall, the values for CONV influent water were higher than the ones for the Post-GAC, as was also demonstrated by the averages per contaminant in Table 3.4B.

Among the contaminants, MTBE had the highest $E_{EO}$ value for both pilot influent water scenarios, while metolachlor and 17α ethynyl estradiol had the lowest $E_{EO}$ values. These $E_{EO}$ values were significantly higher than the values for the LP lamp. This is because the MP technology is less efficient than the LP technology. Many of the wavelengths produced are not used in creating hydroxyl radicals (Ijpelaar et al., 2010). Although there were differences between the $E_{EO}$ values of the various contaminants, the $E_{EO}$ ratio of the CONV to the Post-GAC water varied between 1.2 and 1.6 (See Table 3.4B.). These ratios are slightly lower and the range slightly less than for the LP lamps, suggesting that the efficiency of the MP lamp is less sensitive to variations in NOM.
A. CONV Pilot

B. Post-GAC Pilot Influent
**Figure 3.3:** UV/$\text{H}_2\text{O}_2$ seasonal variation - LP $E_{EO}$ - **A.** CONV, **B.** Post-GAC; - MP $E_{EO}$ – **C.** CONV and **D.** Post-GAC Pilot Influent. From left to right for each contaminant: fall 2007, winter 2008, spring 2008, summer 2008.
Table 3.4A: Average $E_{EO}$ (kWh/m$^3$-order) of contaminants for LP reactor under CONV and Post-GAC water (1 kWh/m$^3$-order = 3.7854 kWh/kgal-order)

<table>
<thead>
<tr>
<th></th>
<th>Atrazine</th>
<th>MTBE</th>
<th>Metolachlor</th>
<th>MIB</th>
<th>EE2</th>
<th>Gemfibrozil</th>
<th>Ibuprofen</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONV</td>
<td>0.30</td>
<td>0.48</td>
<td>0.20</td>
<td>0.20</td>
<td>0.17</td>
<td>0.17</td>
<td>0.27</td>
</tr>
<tr>
<td>Post-GAC</td>
<td>0.18</td>
<td>0.31</td>
<td>0.10</td>
<td>0.12</td>
<td>0.10</td>
<td>0.10</td>
<td>0.17</td>
</tr>
<tr>
<td>$E_{EO}$ Ratio</td>
<td>1.7</td>
<td>1.6</td>
<td>2.0</td>
<td>1.7</td>
<td>1.7</td>
<td>1.6</td>
<td>1.5</td>
</tr>
<tr>
<td>CONV/Post-GAC</td>
<td>1.7</td>
<td>1.6</td>
<td>2.0</td>
<td>1.7</td>
<td>1.7</td>
<td>1.6</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 3.4B: Average $E_{EO}$ (kWh/m$^3$-order) of contaminants for MP reactor under CONV and Post-GAC water (1 kWh/m$^3$-order = 3.7854 kWh/kgal-order)

<table>
<thead>
<tr>
<th></th>
<th>Atrazine</th>
<th>MTBE</th>
<th>Metolachlor</th>
<th>MIB</th>
<th>EE2</th>
<th>Gemfibrozil</th>
<th>Ibuprofen</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONV</td>
<td>0.59</td>
<td>1.42</td>
<td>0.35</td>
<td>0.49</td>
<td>0.31</td>
<td>0.43</td>
<td>0.54</td>
</tr>
<tr>
<td>Post-GAC</td>
<td>0.41</td>
<td>0.90</td>
<td>0.23</td>
<td>0.32</td>
<td>0.25</td>
<td>0.27</td>
<td>0.43</td>
</tr>
<tr>
<td>$E_{EO}$ Ratio</td>
<td>1.4</td>
<td>1.6</td>
<td>1.5</td>
<td>1.5</td>
<td>1.3</td>
<td>1.6</td>
<td>1.2</td>
</tr>
<tr>
<td>CONV/Post-GAC</td>
<td>1.4</td>
<td>1.6</td>
<td>1.5</td>
<td>1.5</td>
<td>1.3</td>
<td>1.6</td>
<td>1.2</td>
</tr>
</tbody>
</table>

UV absorbance scans (200-300 nm) were analyzed through the pilot plant. Figure 3.4 represents scans from the 240 to 300 nm range, the range over which differences between the reactor influent and effluent scans could be observed. The CONV absorbance values (left) were higher than the absorbance values of the Post-GAC (right). This is to be expected because it is well known that GAC tends to reduce the higher molecular weight NOM that would absorb light in the 200-300nm UV absorbance
scans. Clear differences in absorbance are observed before and after UV/H\textsubscript{2}O\textsubscript{2} treatment. (See Figure 3.4.) Based on Korshin et al. (1997), oxidation by chlorination of NOM fractions with high concentrations of hydroxyl, carbonyl, ester, and carboxyl-substituted aromatic rings caused a marked change in the UV scans from 240 to 400 nm. Advanced oxidation by UV/H\textsubscript{2}O\textsubscript{2} would likely create similar reactions. The reduction in the sum of the absorbances (240 – 300 nm) through the UV/H\textsubscript{2}O\textsubscript{2} reactor with CONV pilot influent was consistent, ranging from 23.5 to 27.7%, with the percent reduction being slightly higher in the fall of 2007 and winter 2008 when the overall intensity of absorbance was higher. The range of reduction of absorbances (240 – 300 nm) varied more when the Post-GAC water served as pilot influent, 16.2 to 35.8%. Interestingly, during the summer and fall of 2008, the GAC was least spent, ranging from 75 to 125 run days as compared to an annual average of 150 run days and a maximum of 200 run days and the Post-GAC water had a correspondingly lower UV absorbance. The comparatively greater changes in Post-GAC NOM through UV/H\textsubscript{2}O\textsubscript{2} agreed with the work of Dotson, et al. (2010) who observed 170% increase in 24-hour chlorine demand for GCWW CONV treated water exposed to 1000 mJ/cm\textsuperscript{2} and 10 mg/L H\textsubscript{2}O\textsubscript{2} versus a 273% increase in 24-hour chlorine demand for Post-GAC water. In Dotson’s work, the increase in reactivity of the irradiated NOM was confirmed by an increase in the percentage of total trihalomethane (TTHM) precursor formation after UV/H\textsubscript{2}O\textsubscript{2} treatment, 103% for the CONV water versus 143% for the Post-GAC water. Other researchers have observed that fulvic acids exhibit more reactivity with the hydroxyl radical than humic acids. Pelaez, et al. 2011 reported that scavenging of hydroxyl radical was higher with fulvic acid than humic acid using visible light-activated TiO\textsubscript{2}
photocatalyst. Because fulvic acids are humic acids of lower molecular weight and higher oxygen content (more soluble) than other humic acids, they are less well-removed by GAC. Therefore, it is not surprising that the NOM remaining after GAC adsorption would exhibit more changes in the aromatic character (and conjugated double bonds) as represented by the UV scans, particularly when the GAC was freshly reactivated and removed more of the hydrophobic and higher molecular weight NOM than when it was more spent.
Figure 3.4: UV absorbance scans 240 – 300 nm
MTBE was further studied in laboratory collimated beam experiments. Due to the small molecular size, high solubility and resistance to bioactivity, MTBE is difficult to remove from water. Even though the $E_{EO}$ values for MTBE destruction were relatively high compared to the other compounds studied, advanced oxidation processes are promising technologies for this difficult to remove compound. The UV/H$_2$O$_2$ process has successfully destroyed MTBE, and the kinetics and reaction mechanisms have been well studied (Cooper, 2009). The hydroxyl radicals attack the MTBE molecule through H-abstraction, which can occur from either the methoxy group or any methyl group. The methoxy group of the MTBE molecule is most prone to H-abstraction due to the electrophilicity of hydroxyl radicals and the stereo-electronic effect of the group (Stefan, 2000). Because the UV/H$_2$O$_2$ degradation of MTBE was well understood and the reaction rates calculated, MTBE was an ideal compound for further bench-scale study, relative to NOM effects on the UV/H$_2$O$_2$ process.

Bench-scale experiments were performed using MTBE as the target contaminant to have more control over variables. Figure 3.5 demonstrates the differences in destruction of MTBE over a range of UV doses for the three waters using a collimated beam unit. Water quality greatly influenced the effectiveness of the UV/H$_2$O$_2$ process on the destruction of MTBE. As in the pilot-scale experiments, the water with higher concentrations of NOM required a higher UV dose to achieve the same destruction of MTBE than water with lower concentrations of NOM. UV/H$_2$O$_2$ was more efficient in water with lower TOC and SUVA values, as there is less competition from scavengers for hydroxyl radicals. In addition, more hydroxyl radicals were formed at a lower dose in water with less humic content, because there was less absorption of UV light by the
humic material, which made more UV light available to produce hydroxyl radicals. To achieve 60% destruction, RO water (TOC averaging 0.0331 mg/L) required a dose of 380 mJ/cm². Post-GAC water, which has TOC concentration averaging 0.85 mg/L, required 600 mJ/cm². CONV water with the highest NOM concentration (TOC averaging 1.77 mg/L) and SUVA value (highest humic to non-humic ratio) required a dose of 1100 mJ/cm² to achieve 60% destruction. The efficiency of MTBE destruction in CONV water was 54% less than in Post-GAC water (600 versus 1100 mJ/cm² required).

**Figure 3.5: MTBE Destruction with Varying Water Quality – Collimated Beam**

Figures 3.6A and 3.6B depict the relationship between MTBE destruction and TOC for 600 mJ/cm² and 1000 mJ/cm², respectively. Note that at both UV doses, destruction decreased as TOC increased, but that the correlation was somewhat more linear and had less scatter at 1000 mJ/cm² than at the 600 mJ/cm². At the 1000 mJ/cm² there was enough UV energy to overcome more of the UV absorbance and scavengers at higher
TOC levels. Figures 3.6C and 3.6D depict the correlation between MTBE destruction and SUVA for 600 mJ/cm² and 1000 mJ/cm², respectively. A linear relationship between destruction and SUVA was observed at both UV doses $R^2$ of .84 and 0.87 for the 1000 mJ/cm² and the 600 mJ/cm² doses, respectively. Because SUVA represents a ratio of UV$_{254}$ absorbance to TOC, it is a measure of the type of NOM rather than the concentration. The UV light emitted by the low pressure lamp was emitted at 254 nm. So absorbance at this wavelength reduces UV effectiveness.
Figure 3.6: MTBE Destruction: A. Varying TOC (mg/L) 600 mJ/cm$^2$ B. Varying TOC (mg/L) 1000 mJ/cm$^2$ C. Varying SUVA L/mg-m 600 mJ/cm$^2$ D. Varying SUVA L/mg-m 1000 mJ/cm$^2$
Figures 3.7A (collimated beam) and 3.7B (pilot-scale) demonstrate the correlation between TOC and $E_{EO}$ for a wide range of water quality conditions and UV doses (500-1300 mJ/cm$^2$ for the pilot plant and 0 to 1200 mJ/cm$^2$ for the collimated beam experiments). Although the collimated beam data and the pilot-scale data cannot be directly compared, it is obvious that the collimated beam data exhibits better linear correlation $R^2$ of 0.86 vs. 0.58. Some authors have observed a pseudo first order reaction for UV/H$_2$O$_2$ destruction. Even though second order rate constants have been developed for MTBE, under some conditions a pseudo-first order reaction can be assumed for many UV/H$_2$O$_2$ contaminant destruction reactions. Since $E_{EO}$ is calculated on a per order of destruction, a linear relationship would be expected. $E_{EO}$ values in the pilot were also higher than in the collimated beam demonstrating less efficiency in the pilot-scale reactor. But again the two values are not comparable because, the power calculation for the collimated beam represents an idealized laboratory situation. For these experiments, the power that the LP lamp imparted to the water was calculated as the product of the fluence rate (irradiation) and the exposure time as per Bolton and Linden (2003). However, absorbance was removed from the equation because it is a factor that causes energy demand. Likewise, absorbance was not considered in calculating the power term for $E_{EO}$ values of the pilot-scale process.
Figure 3.7: Correlation TOC (mg/L) vs. $E_{EO}$ – A. Collimated Beam B. Pilot Plant; Correlation SUVA (L/mg-m) vs. $E_{EO}$ – C. Collimated Beam D. Pilot Plant

Figures 3.7C and 3.7D demonstrate the linear correlation between SUVA and $E_{EO}$ for the same range of UV doses. Figure 3.7C presents the collimated beam data, while Figure 3.7D presents the pilot plant data. Less UV$_{254}$ data was available than TOC data for the pilot, so fewer SUVA values could be calculated for the pilot plant than TOC concentrations. Very good linear correlation was determined for the pilot plant and the collimated beam data, R$^2$ of 0.89 and 0.92, respectively. Again SUVA indicates the type of NOM, which plays a very important role in determining UV absorption, as hydroxyl radical scavenging is likely influenced by the type of NOM.

Crittenden et al., (1999) developed a comprehensive model for predicting contaminant destruction by UV/H$_2$O$_2$, the AdOx™ Model. For this present study, MTBE destruction
was modeled (based on collimated beam data using average SUVA conditions for each water) to determine the NOM rate of reaction for RO, Post-GAC and CONV waters. The following inputs are required: reactor type, volume, initial hydrogen peroxide dose, pH, alkalinity, NOM (g mol/L), initial target contaminant concentration (4.54 x 10^-8 g mol/L), lamp power, UV path length, UV light intensity, empirically determined NOM extinction coefficient ((mg/L)^-1(cm)^-1), second order rate constant for the target contaminant (1.6 x 10^9 M^-1 s^-1 as published by Kavanaugh et al., (2003)). The NOM second order rate constant for the experimental collimated beam data was then determined for each water by trial and error. It is important to note that the influence of humic substances on hydroxyl radicals scavenging and adsorption of UV light are considered in the model. However, the influence of the photolysis of humic acid and the formation of by-products by humic degradation are not considered.

In order to determine the NOM concentration for the purposes of this model, it is important to know the percent carbon of the natural organic matter. Four concentrated and freeze dried samples of raw and filtered water NOM processed as per Pressman et al., (2010) and McCurry, et al. (2012) were analyzed for elemental analysis (Huffman Laboratory, Golden, CO). The C represented 50 to 53% of the organic material composition through the plant and 52 to 53% in the filtered water. Therefore, these were the value used in the modeling runs. Figures 3.8A, 3.8B and 3.8C depict the model runs vs. the experimental collimated beam data. Figure 3.8A represents the RO water and the best-fit model run, after varying NOM rate of reaction. For RO water with very low TOC and SUVA, the second order NOM reaction rate was 1.7 x 10^8 M^-1 s^-1. Figures 3.8B and 8C represent Post-GAC water and the CONV water, respectively. The best fit
model for the second order NOM reaction rate was $1.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$. Westerhoff et al., (2007) used pulse radiolysis experiments to determine the average second-order rate constants for reactions between NOM and the hydroxyl radical. Suwannee River standard fulvic acid had a reaction rate of $1.6 \pm 0.24 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$. This value is very similar to the RO treated water. The reaction rates for the CONV and Post-GAC NOM (with average SUVA values) from this present study were similar to Westerhoff’s lowest values for natural water $1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$. Again, the water with the least NOM (the RO water) has the highest value for the second order NOM reaction rate. Empirical alkalinity and pH values were used in the model. The RO membrane removed the higher molecular weight compounds more efficiently, passing the small and potentially more reactive NOM. Drewes et al., (2003) found that RO could efficiently reject high molecular weight NOM characterized as humic and fulvic acids. But, approximately 40–50 percent of the permeate TOC was comprised of low molecular weight acids and neutrals with a molecular weight of 500 Daltons or less.
Figure 3.8: AdOx™ Model and Collimated Beam Experimental Data  
A. Reverse Osmosis Water;  B. Post-GAC Water;  C. CONV Water
3.4. Summary and Conclusions

- Higher NOM resulted in a higher $E_{EO}$ for UV/H$_2$O$_2$ target contaminant destruction. The $E_{EO}$ ratios between the CONV and Post-GAC water range between 1.5 and 2.0 for the seven compounds studied. Higher NOM increased the $E_{EO}$ similarly for these compounds.

- Water through the UV/H$_2$O$_2$ process exhibited a change in UV absorbance from 240 to 300 nm, with the reactor effluent having less absorbance than the influent at all wavelengths. The CONV water had a more consistent percentage change, even though the overall absorbance was higher. The Post-GAC water exhibited a wider range of change. The pilot influent that represented newly reactivated GAC, exhibited the greatest change in NOM, suggesting that the GAC non-adsorbable fraction of NOM was the most reactive relative to aromatic destruction or fragmentation.

- MTBE destruction by UV/H$_2$O$_2$ correlated very well with SUVA values, indicating the importance of the type of NOM.

- $E_{EO}$ for the destruction of MTBE also correlated well with SUVA values for both the pilot-scale and bench-scale experiments

- Second order NOM reaction rate for the CONV and Post-GAC calculated using the AdOx™ model was $1.0 \times 10^8$ M$^{-1}$s$^{-1}$. The second order NOM reaction rate for the very low NOM RO water was $1.7 \times 10^8$ M$^{-1}$s$^{-1}$ for MTBE destruction, suggesting that the lower molecular weight NOM pass the membrane was more reactive than the CONV and Post-GAC waters at the time they were sampled.
3.5. Acknowledgements

We appreciate the help of Karl Linden from University of Colorado, Boulder, in designing the collimated beam unit. We also appreciate the help of Aaron Dotson from the University of Alaska, Paul Westerhoff from the University of Arizona and Jonathan Pressman from the USEPA Research Center. We would like to acknowledge the support of KWR Watercycle Research Institute, the Dutch Ministry of Economic Affairs and the Water Research Foundation for their support of this research. Special thanks to the Greater Cincinnati Water Works Water Quality and Treatment and Supply Divisions.

3.6. References


SRC Environmental Science Database (2007) North Syracuse, NY.


Chapter 4

The Effect of UV/H$_2$O$_2$ Treatment

on Biofilm Formation Potential
The efficacy of ultraviolet light/hydrogen peroxide advanced oxidation (UV/H$_2$O$_2$) was evaluated for reducing trace organic contaminants in natural water with varying water qualities. A year long UV/H$_2$O$_2$ pilot study was conducted to examine a variety of seasonal and granular activated carbon (GAC) breakthrough conditions. The UV pilot-scale reactors were set to consistently achieve 80% atrazine degradation, allowing comparison of low pressure (LP) and medium pressure (MP) lamp technologies for by-product formation. Because hydroxyl radicals react non-selectively with organic compounds, unintended by-product formation occurred.

Total assimilable organic carbon (AOC) concentration increased through the reactors from 14 to 33% on average, depending on water quality. Natural organic matter (NOM) contains the precursors for AOC production, so when post-GAC water (versus conventionally treated water) served as reactor influent, less AOC was produced. No appreciable difference in AOC concentration was observed between LP and MP UV reactors. The *Spirillum* strain NOX fraction of the AOC increased from 50 to 65% on average, depending on the quality of the water. The increase in this fraction of AOC occurred because oxidation of NOM yielded smaller more assimilable organic compounds such as organic acids that are necessary for NOX growth. The *Pseudomonas fluorescens* strain P17 AOC concentration increased only when conventionally treated plant water was used as pilot influent. This organism thrives in waters of differing organic energy sources, but does not thrive well in carboxylic acids alone. The CONV water had more overall TOC that could contribute to higher P17 AOC counts.

Biofilm coupon studies indicated that biofilms with greater heterotrophic plate counts were observed in the granular activated carbon (GAC) effluent streams receiving UV/H$_2$O$_2$ pretreatment. Biofilm coupon studies additionally indicated that the effluent stream of the GAC column proceeded by the MP reactor exhibited more viable biofilm than the other GAC effluent streams based on an ATP bioluminescence method. The increased viability of the biofilm produced by the MP UV reactor is likely a result of the multiple UV wavelengths and higher energy input characteristic of this technology.
4. The Effect of UV/H\textsubscript{2}O\textsubscript{2} Treatment on Biofilm Formation Potential

4.1. Introduction

Greater Cincinnati Water Works (GCWW) is designing a 908,500-m\textsuperscript{3}/d (240-MGD) ultraviolet (UV) disinfection facility to be constructed by early 2012 at their Ohio River drinking water plant. GCWW additionally wished to determine the efficacy of ultraviolet light/hydrogen peroxide advanced oxidation process (UV/H\textsubscript{2}O\textsubscript{2}) for reducing pharmaceuticals and other organic contaminants at two points in the treatment process. A twelve-month UV/H\textsubscript{2}O\textsubscript{2} study was conducted in order to cover seasonal variations and different levels of granular activated carbon (GAC) breakthrough. Low pressure (LP) and medium pressure (MP) UV lamp technologies were able to be compared for by-product formation, because the pilot-scale systems were normalized for 80\% atrazine destruction. Two plant-process sources with varying natural organic composition and concentration were compared for UV/H\textsubscript{2}O\textsubscript{2} and UV photolysis (without hydrogen peroxide) technologies. The enhanced removal of natural organic matter with UV/H\textsubscript{2}O\textsubscript{2} followed by biologically active GAC was also evaluated. Biofilm formation potential was investigated through the UV/H\textsubscript{2}O\textsubscript{2} reactors and through GAC following UV/H\textsubscript{2}O\textsubscript{2} process.

UV/H\textsubscript{2}O\textsubscript{2} is a promising technology for the destruction of endocrine disrupting compounds (EDCs) and pharmaceuticals and personal care products (PPCPs), which combines the effects of direct and indirect UV photolysis (Pereira et al, 2007). Direct photolysis takes place when a compound absorbs photons of an energy level capable of breaking down bonds (Hovorka et al, 2001). Medium pressure lamps are more energy-intensive and emit a broad-spectrum of UV wavelengths, thus achieving direct UV
photolysis at multiple wavelengths. Low pressure UV lamps primarily emit UV at 253.7 nm, and only achieve direct UV photolysis at this wavelength (Rosenfeldt, 2004). Light absorption behavior and direct UV photolysis of organic contaminants, however, is also a function of radiation wavelength. So, different wavelengths could influence the type, selectivity and yields of by-products formed.

Indirect UV photolysis with hydrogen peroxide (H$_2$O$_2$) results in the cleavage of the HO-OH bond, causing the formation of hydroxyl radicals (-OH). Although the UV absorption coefficient of H$_2$O$_2$ is a function of UV wavelength, both LP and MP UV lamps emit wavelengths that can cause photolysis of H$_2$O$_2$ to generate hydroxyl radicals. UV photolysis of H$_2$O$_2$ is a rapid process and the produced hydroxyl radicals react non-selectively with organic compounds yielding carbon-centered radicals. They target mainly unsaturated bonds or abstract hydrogen from C-H bonds (Buxton, 1988) especially those in α-position to π-systems, amines, ethers, thioethers, and carbonyl compounds (Hovorka et al, 2001). These carbon-centered radicals in turn rapidly react with dissolved oxygen to form peroxyl-radicals, followed by the breakdown of peroxyl radicals to form oxyl-radicals, and the breakdown of oxyl-radicals to other radicals and stable reaction intermediates (Hovorka et al., 2001). In UV/H$_2$O$_2$ systems many radical-based reactions take place (i.e., generation, propagation, termination). The efficiency of the process is dependent upon the rate of formation of hydroxyl radicals, the presence and concentrations of hydroxyl radical scavengers and other parameters (i.e., UV absorbance of the process water, type and concentration of other organic impurities in water such as natural organic matter, type and concentration of target organic contaminants, water temperature) (Antoniou et al., 2009). The most prominent
scavengers are the dissolved organic compounds (DOC), and alkalinity (HCO$_3^-$, CO$_3^{2-}$), however, H$_2$O$_2$ will also react with hydroxyl radicals (Pereira et al., 2007).

The pilot-scale systems included GAC columns to adsorb and potentially biodegrade intermediates and by-products. Organic biodegradation can be advantageous in drinking water treatment, and is usually accomplished through the soil and dunes as pre-treatment or through biologically active filtration or GAC. But, biodegradable organics leaving the plant can cause microbial regrowth in the distribution system, a potentially serious problem. Weinrich et al., (2009) states “In distributed water, bacterial regrowth is perhaps the most significant mechanism for water quality deterioration between the treatment plant and the end user.” Coliform bacteria and pathogenic organisms can grow and be shielded in the biofilm and be difficult to eliminate. Biofilms can be responsible for disinfectant depletion and problems with taste and odor. In chloraminated systems nitrification may also occur. Even corrosion rate can be increased by the presence of biofilm under certain conditions (Geesey et al., 1989).

Distribution system biofilm growth is caused by a combination of factors. Generally, four water quality parameters control microbial regrowth: temperature, assimilable organic carbon (AOC), availability of nutrients (trace inorganic compounds) and residual disinfectant presence (Reasoner et al., 1991). However, LeChevallier et al., 1996, investigated coliform regrowth in 31 drinking water systems. Their conclusion was that there was a complex interaction of physical, chemical operational and engineering factors involved in bacterial regrowth. Temperature, particulate protection of microorganisms, types of organisms colonizing the distribution system (e.g., resistance of microbes to disinfection) and nutrient concentrations are factors controlling the type
and amount of biofilm (Baribeau et al., 2005). Kaplan et al., 2004 determined that source waters possess widely different quantities and qualities of biodegradable organic as carbon sources, and these differences in organics influence the community of heterotrophic bacteria in biofilm.

Drinking water sources contain various levels of natural organic matter (NOM). While the composition of NOM varies from location to location, there are some similarities in the structure. Humic substances comprise up to 75% percent of the NOM (Volk et al., 1997). Organic matter originating from soils is derived from plant matter, which has a high lignin content. Lignin has a predominant aromatic fraction. NOM also provides reduced carbon that supplies energy and carbon for bacterial metabolism (Kaplan et al., 2004). Kaplan and Gremm (1995) determined 54% of the most biodegradable material in the waters sampled was humic in nature. Butterfield and colleagues (1997) additionally found that humic substances in the distribution system were the primary carbon source supporting distribution biofilm. However, while the formation of biofilms in the distribution system is believed to be ubiquitous, the degree of colonization varies from site to site.

Research to determine the exact chemical composition of biodegradable organic matter is on-going. It is known that lower molecular weight compounds are more easily transported across cell membranes enabling enzymatic reactions to proceed. Assimilable organic carbon (AOC) is often used to quantify regrowth potential and to gain insight into the types of compounds comprising biologically degradable carbon. The AOC method developed by van der Kooij in 1982, 1984 makes use of two specific strains of organisms that allow for universal comparison of biofilm potential among
diverse utilities. *Pseudomonas fluorescens* strain P17 is able to utilize various compounds such as proteins, amino acids, carbohydrates, alcohols and aromatic acids, but does not grow well in carboxylic acids alone (LeChevallier et al., 1993). It has great nutritional variability. *Spirillum* strain NOX is more selective in its growth substrates. Only carboxylic acids and a few amino acids promote growth of NOX. In situations such as ozonation where compounds not utilized by P17 are present, *Spirillum* strain NOX is often used. Carboxylic acids promote more rapid growth of NOX than P17, thus NOX growth is a more sensitive indicator of the presence of these compounds. Also, in cases of low AOC, this organism tends to grow better than P17. Therefore, this method can be used to obtain information about the quantity and chemical composition of the assimilable materials (AwwaRF and KIWA, 1988). Van der Kooij (1992) has recommended that unchlorinated systems maintain AOC values below 10 µg/L. Lechevallier et al., (1990 and 1996) however, provided evidence that chlorinated systems may limit regrowth and coliform occurrence by maintaining AOC less than 50 to 100 µg/L. Shi-hu et al., (2008) found that the AOC/TOC ratio increased with decreasing apparent molecular weight (MW). Hem and Efraimsen 2001 found 50-70% of the AOC fraction were <1000 Daltons molecular weight. Other researchers observed good correlation between apparent molecular weight distribution (AMWD) and UV absorbance (at 254 nm) to TOC ratio and biodegradability of raw waters (Goelet et al., 1995). The AOC fraction is generally less than 1,000 MW, Hem and Efraim (2001), and can include sugars, fatty acids, amino acids and peptides (Haddix, et al, 2004). These results would confirm the simpler lower MW fractions would be the most assimilable by biodegrading micro-organisms.
The UV/H$_2$O$_2$ process forms hydroxyl radicals that react non-selectively. Organic free radicals then can form small MW fractions such as aldehydes, ketones, alcohols, and carboxylic acids that can be used in microbial metabolism (Speitel et al., 1999). Wu (1991) studied the biodegradation of commercial humic acid after UV/H$_2$O$_2$ treatment. Wu was able to increase biodegradability by 17%. Biodegradable dissolved organic carbon (BDOC) increased from 0.1 to 1.3 mg/L in Lake Austin Water in continuous flow UV/H$_2$O$_2$ experiments and 0.52 to 0.87 mg/L in Lake Houston Water. Acetic and oxalic acids are often found as intermediates of the NOM oxidation process, and these acids biodegrade readily (Speitel et al., 1999).

GAC has been used for the adsorption of organic compounds in drinking water. Organic adsorption onto GAC is known to be influenced by several variables including pore size distribution, internal surface area, GAC surface functional groups, electrostatic interactions, acidity, ash content, the size shapes and properties of the organic compounds and the pH, dissolved oxygen and ions in solution (Moore et al., 2004). In general, less soluble organic compounds (hydrophobic) are better adsorbed than soluble compounds (hydrophylic). Therefore, polar compounds, which tend to be hydrophilic, are less well adsorbed than non-polar compounds. Westerhoff et al., (2005) found a correlation between log $K_{ow}$ (measure of hydrophobicity) and the removal of 22 pharmaceutical and personal care products.

Because of the surface area created by pores, GAC provides an excellent substrate for biological activity. GAC pores provide protection from shear forces and the functional groups of the adsorbed organic material provides a mechanism for chemical binding (Carvalho, 2001). Also, biofilms on a fixed media are less affected by organic loading.
changes than are suspended growth systems. Studies have shown that biologically active carbon can continue to be effective even when contaminant levels were low (Shi et al., 1995). This pilot study examined the use of GAC before and after the UV/H\textsubscript{2}O\textsubscript{2} process.

4.2. Methods

4.2.1. Facilities

The source water for the UV/H\textsubscript{2}O\textsubscript{2} pilot influent was drawn from two locations within Greater Cincinnati Water Works’ (GCWW) Ohio River treatment plant. The first location was after coagulation, settling and filtration, i.e., conventional treatment (CONV). The second location was from the GAC adsorber effluent (Post-GAC). Water exiting the filters was sent to the granular activated carbon (GAC) facility. The GAC contactors were filled with 11.4 ft (3.5 m) of carbon and were operated in a down-flow, gravity mode. Carbon contact time averaged about 20 minutes during the study.

The GAC removed a broad spectrum of organic compounds present in the Ohio River. Water entering the GAC facility had a TOC averaging 1.86 mg/L; water exiting the facility had a TOC averaging 0.89 mg/L. The GAC facility also served to significantly reduce disinfection by-product precursors and biodegradable organic carbon.

After becoming exhausted (average combined effluent of 150 days, maximum combined effluent 200 days), the GAC was thermally reactivated onsite. This carbon treated water was used as the second of the two pilot influent process streams (Post-GAC process stream).
A schematic of the full-scale process train, indicating these locations is shown in Figure 4.1.

Figure 4.1: Schematic of the Richard Miller Treatment Plant - Cincinnati, Ohio, U.S.A.

Table 4.1 presents the pertinent water quality data for the two pilot influent streams. The organic parameters of the CONV pilot influent stream were more variable than those of the Post-GAC pilot influent stream. Temperature, alkalinity and anions did not change through the GAC adsorption process.
Table 4.1: Water quality of CONV and Post-GAC water at RMTP – Pilot Plant Influent

<table>
<thead>
<tr>
<th>Water Quality Parameter</th>
<th>CONV</th>
<th>Post-GAC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Minimum</td>
</tr>
<tr>
<td>pH</td>
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<td>7.2</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
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<td>1.22</td>
</tr>
<tr>
<td>UV&lt;sub&gt;254&lt;/sub&gt; (L x cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
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<td>0.024</td>
</tr>
<tr>
<td>Total Alkalinity (mg/L as CaCO&lt;sub&gt;3&lt;/sub&gt;)</td>
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<td>49</td>
</tr>
<tr>
<td>Temperature</td>
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</tr>
</tbody>
</table>

4.2.2. Pilot Plant Design and Operation

GCWW’s pilot plant consisted of a constant head tank, the peroxide and contaminant feed systems, the UV reactors, the GAC column skids, and the annular reactors. Figure 4.2 depicts the layout of the pilot including the location of the chemical injection and sampling points.

CONV or Post GAC water was pumped by centrifugal pumps into the 600 L (160 gal) polyethylene constant head tank. The constant head tank was located about 6 m (20 feet) above the UV reactors to provide sufficient head for the water flow through the unit. The water flow split into two lines before entering the UV reactors.

The atrazine solution and the 8% hydrogen peroxide solution were injected through two PVC inline injection mixers located three feet apart to ensure complete mixing. The contaminant solution was pumped from a polypropylene 19 or 115 L (5 gal or 30 gal) tank through a diaphragm pump into the inline mixer. The hydrogen peroxide was
diluted down to 8% and was fed continually through a positive displacement pump and the second mixer. A 2 µg/L atrazine concentration and a 10 mg/L H₂O₂ were targeted.

The LP reactor (Aquionics model ALT320 TOC reduction range) consisted of eight LP lamps oriented parallel to the central axis and placed equidistantly at about a 11 cm radius from that axis. The reactor’s internal diameter was about 31 cm and its chamber length is approximately 97 cm. The 80 W LP lamps and sleeves were standard disinfection models from Aquionics with an expected lifetime for the lamps of 12,000 hours. The reactor included an immersed pre-calibrated UV monitor (Hanovia) sensitive to UVC wavelengths. A display on the power supply box indicated the UV intensity, run hours, and on/off lamps. The flow range through the reactor could vary between 1.8 to 10 m³/hr (8 to 44 gpm).

The MP reactor (Aquionics model Photon II TOC reduction range) consisted of one MP lamp oriented parallel to the flow, and could be operated at 4 power levels ranging from 75 to 100% of the power. The reactor’s internal diameter was about 15 cm and its chamber length is approximately 97 cm. The 3.5 kW MP lamp and sleeve were Super TOC models from Aquionics with an expected lifetime for the lamp of 8,000 hours. The reactor included an immersed pre-calibrated UV monitor (Hanovia) sensitive to UVC wavelengths, and a manual rubber wiper. A digital display on the power supply box indicated the UV intensity, UV dose, run hours, and temperature, and allowed for flow and UVT₂₅₄ input for the computation of the UV dose. The flow range through the reactor could vary between 1.8 to 10 m³/hr (8 to 44 gpm).

The effluent from both UV reactors and the control water (pilot influent water before the hydrogen peroxide injection point but after the contaminant injection point) were
pumped to four GAC pilot columns. Two GAC columns were fed by the control water, control columns 1 and 2. Each of the remaining two columns received the effluent of the LP reactor or the effluent of the MP reactor. The GAC columns contained reactivated GAC acquired directly from the reactivation facility at Richard Miller Treatment Plant (RMTP) Cincinnati, Ohio. The GAC was bituminous coal, US mesh size 12x40 with 0.55-0.75mm effective size, and apparent density of 0.48 g/cm$^3$ (30 lbs/ft$^3$). The GAC bed depth in the 10.2 cm (4 inch) diameter columns was about 173 cm (68 inches), yielding an empty bed contact time of 15 minutes.

Finally, four annular reactors (Biosurface Technologies, model 1120 LS) were connected to the effluent lines of the GAC columns as shown in Figure 4.3. The annular reactors were chosen to simulate a velocity of a typical water distribution main and are described further in the analytical methodologies section.
Figure 4.2: Pilot plant process at GCWW
The pilot study was structured to address the multiple research objectives within a period of 12 months. The pilot unit was constructed in the summer of 2007 and the tests began in the fall of 2007. During each quarter there were three phases of testing: (a) UV/H$_2$O$_2$ with CONV influent water, (b) UV/H$_2$O$_2$ with Post-GAC influent water, and (c) UV photolysis with Post-GAC influent water. For both UV/H$_2$O$_2$ phases the operation of the system was based on performance. The goal was to operate the UV/H$_2$O$_2$ system so that atrazine would degrade by 80% through both the LP and MP reactor trains. The
hydrogen peroxide concentration was maintained at 10 mg/L at all times (except during the UV photolysis testing) and the UV dose was adjusted by changing the flow through the reactors, and for the MP reactor by adjusting the power levels. Since the ultraviolet transmittance at wavelength 254 nm (UVT$_{254}$) and TOC concentration of the water varied seasonally, tests were performed at the beginning of each phase using atrazine to determine the operational conditions of the UV reactors. An 80% atrazine was targeted for the UV/H$_2$O$_2$ phases to determine the operational conditions of the UV reactors. This protocol was followed during both CONV and Post-GAC pilot influent conditions. Following the Post-GAC UV/H$_2$O$_2$ phase, the hydrogen peroxide feed was discontinued, the UV dose at the reactors was set at the lowest level and the spiking was repeated. During this time period atrazine destruction of 80% was not achievable. When the three phases were completed, the pilot influent was switched to CONV water and the reactors and flows were set at the 80% atrazine degradation conditions until the next quarter began.

During the 12 month study several water quality, operational and performance parameters were monitored for the pilot. The pilot was monitored on a daily basis for flows, UV reactor intensity and applied UV dose. The UVT$_{254}$ of the pilot influent was monitored and the hydrogen peroxide concentration was determined before and after the reactors and after the GAC contactors. Additionally, several other water quality parameters, such as TOC and alkalinity were tested at various frequencies across the pilot. The analytical methods for these tests were from the American Public Health Services Standard Methods for the Examination of Water and Wastewater. (See Appendix Table C.1.)
4.2.3. Analytical Methodologies

AOC was one of the methods used to assess biofilm formation potential. The analytical method performed was from the 9217B American Public Health Services Standard Methods for the Examination of Water and Wastewater. (See Appendix Table C.1.) The AOC test has been found to be a useful tool for predicting bacterial growth in the distribution system. However, it should be noted that carbon is not always the limiting nutrient (LeChevallier 1987 and 1991). Additionally, other distribution conditions are not considered.

Annular reactors were used to assess biofilm potential after GAC adsorption in unchlorinated process streams as per Sharp et al. (2001). (See Figure 4.3.) Four model 1320LS Laboratory Annular Reactors from BioSurface Technologies Corp. received flow from the effluent of the four GAC columns. The experiment ran from September 4, 2008 to October 2, 2008, which corresponded to run-day 300 to 328 of the GAC. The sterilized annular reactors were reassembled on site with motors and controllers and set to a flow rate of 8 mL/minute and a carousel rotational speed of 90 revolutions per minute. These conditions simulated a pipe velocity of 0.30 meters per second (1 foot/second). The biofilm was quantified by heterotrophic plate count (Standard Methods 9215 B) and ATP bioluminescence analysis. The bioluminescence methodology is based on detection of adenosine -5'-triphosphate (ATP) in metabolically active cells. A luminometer was used to quantify the ATP bioluminescence. It gives a direct measurement of the light intensity and therefore a direct quantification of ATP. The light is quantified as relative light units (RLU), and the intensity of the emission is proportional to the concentration of ATP. Bioluminescence was measured using a
Hygiena System SURE Plus luminometer. The annular reactor methodology and the microbial tests are described in more detail in Appendix C.

4.3. Results and Discussion

4.3.1. Background Water/operational

The pilot unit was in continuous operation from October of 2007 until October 2008. During that period the pilot influent water showed seasonal variations or changes in water quality due to natural surface water fluctuations and the upstream treatment processes. The influent water quality parameters potentially affecting the performance of the UV advanced oxidation process were UVT$_{254}$, TOC concentration, alkalinity and iron concentration. Influent UVT$_{254}$ and TOC concentration were expected to fluctuate during the year, especially for the CONV pilot influent water, which was used most of the time during the pilot study.

The changes in UVT$_{254}$ for the CONV and the Post GAC water can be seen in Figure 4.4. The CONV water UVT$_{254}$ ranged between 84 and 95%/cm, with its lowest points being in December 2007 and the summer of 2008. The UVT$_{254}$ of the Post-GAC water was more stable and fluctuated only between 95-98%/cm. The variation in UVT$_{254}$ greatly affected the operation of the UV reactors and changes in flow and power level were required in order to achieve the required 80% atrazine degradation.
The TOC concentration of the pilot influent water also varied over the 12 month study, fluctuating between 1.2-2.6 mg/L for the CONV water and 0.6-1.0 mg/L for the Post-GAC water. On average a slight 2-3% decrease in TOC concentration was observed through both reactors when CONV was the pilot influent water. When Post-GAC pilot influent water was used, the decrease in TOC concentration through the reactors averaged 4-7%. These consistent small decreases in TOC concentration through the UV reactors can be explained by the partial mineralization of natural organic matter (NOM) by the hydroxyl radicals formed in the reactors. Due to their redox potential of 2.8V, hydroxyl radicals have the potential of completely oxidizing organic molecules to carbon dioxide (Carr and Baird, 2000). Research has shown that under advanced

Figure 4.4: UV Transmittance of CONV and Post GAC water during study
oxidation conditions similar to the ones applied in this study, NOM was not mineralized, but partially oxidized, resulting in a shift of molecular weight distribution towards smaller organic molecules. However, when pre-treatment processes remove higher molecular weight fractions of NOM (as indicated by the drop in specific ultraviolet absorbance (SUVA) values), then UV/H₂O₂ at similar conditions used in this study may cause mineralization of NOM (Sarathy and Mohseni, 2007 and 2009). The CONV pilot influent water had been coagulated, flocculated and filtered which decreased the TOC concentration by 30% (from 2.5 to 1.7 mg/L), and SUVA by 25% (from 3.4 to 2.6 L*mg⁻¹*M⁻¹) on average, while GAC adsorption reduced the TOC concentration of the raw water by 65% (from 2.5 to 0.85 mg/L), and the SUVA value of the raw water by 50% (from 3.4 to 1.7 L*mg⁻¹*M⁻¹). The reduction in TOC and SUVA values between the river, CONV, and Post-GAC water is likely the reason that mineralization of TOC was observed through the UV reactors during the UV/H₂O₂ process.

Figure 4.5 represents TOC concentration through the pilot plant, including the effluent of the GAC pilot columns when CONV water was used as the pilot influent. The top three curves depict CONV influent TOC concentration and the two UV/H₂O₂ reactor effluent TOC values. The bottom four curves represent TOC concentrations for the GAC column effluent streams from the LP and MP reactor process trains and the two control GAC columns. Typical breakthrough curves were observed for all four GAC pilot column effluent streams. TOC concentration in the GAC effluent streams ranged from 0.2 to 1.6 mg/L over the study period. At the beginning of the GAC pilot column runs, there was excellent TOC removal, and over the first 140 to 150 days as the GAC became loaded with organics, the effluent TOC concentration exhibited a rising trend, even though the
influent TOC concentration was declining. Steady-state was reached between 140 to 160 days. After this point, the GAC effluent TOC concentrations reflect the increases and decreases of the TOC concentration in the GAC influent. However, some removal was observed through all GAC columns during the study period. By run day 220 there was a clear separation in the TOC concentrations of the GAC effluent streams that had received UV/H₂O₂ pretreatment and those that had not as shown in Figure 4.6. Overall, the GAC effluent following the UV/H₂O₂ reactors resulted in 8 % less TOC concentration than the control GAC effluent streams. After GAC run day 220, the GAC effluent following the UV/H₂O₂ reactors averaged 16 % less TOC concentration than the GAC effluent of the control process streams. It should be noted that after GAC run day 220 the water temperature was the warmest (26 to 29°C), reflecting summer conditions (June 18, 2008 to August 27, 2008). It is therefore likely that enhanced TOC concentration removal was attributable to more bioactivity caused by the warmer temperatures and more assimilable materials loaded onto the GAC after UV/H₂O₂ treatment. When UV/H₂O₂ is employed, changes to the molecular structure of dissolved organic matter occur. Larger molecules are fragmented into smaller molecular weight compounds and a decrease in aromaticity results. Additionally, the ratio of hydrophilic to hydrophobic compounds increases (Sarathy et al., 2007 and 2009). Smaller molecules of a hydrophilic nature tend to be more assimilable by microorganisms and thus more biodegradable.
Figure 4.5: TOC through pilot-CONV influent
4.3.2. Atrazine Normalization

A primary operational goal of the pilot study was to consistently set the UV reactors at the proper UV dose that would achieve the benchmark 80% atrazine degradation. This became particularly challenging when CONV influent water was used, since the UVT \textsubscript{254} of the water fluctuated significantly throughout the year, and different UV doses were required to keep the atrazine degradation constant. To achieve these conditions throughout the study UV doses between 1200-2000 mJ/cm\textsuperscript{2} were required for the LP reactor (based on the manufacturer’s UV dose tables) and 200-500 mJ/cm\textsuperscript{2} were required for the MP reactor. Atrazine reduction was between 75-85% for most of the study quarters, with the only exception being the first quarter of the study when it was measured at 62% for the LP reactor. The reason for the low value the first quarter was
likely iron fouling of the LP reactor sleeves because of an improperly primed pump. After the sleeves were cleaned the LP reactor could provide sufficient UV dose to reach the benchmark.

When the higher UVT_{254} Post-GAC water was used as influent to the pilot reactors, adjustments to their flow and power level were made to reach the 80% atrazine degradation conditions. These conditions were met closely for both reactor types for almost all study quarters.

In addition to the UV/H_{2}O_{2} experiments, tests were performed to examine the degradation of contaminants by photolysis using Post-GAC as pilot influent. Since the two reactor types could provide significantly different UV dose ranges, the photolysis tests were performed at the low end of UV doses for each reactor, which were around 800 mJ/cm\(^2\) for the LP reactor (as estimated by the supplier’s UV dose tables) and 280 mJ/cm\(^2\) for the MP reactor.

4.3.3. Biofilm Formation Potential

4.3.3.1. Assimilable Organic Carbon (AOC) through UV/H_{2}O_{2} Pilot

Non-chlorinated AOC samples were collected throughout the pilot run to reflect variations in water quality in the process streams when the pilot was normalized for 80% atrazine destruction. When using the CONV process stream as influent to the pilot plant, the total AOC concentration increased through the UV/H_{2}O_{2} reactors from an average of 106 µg/L, to an average of 141 µg/L (33% increase) for the LP process train and from an average of 106 µg/L, to an average of 137 (30% increase) for the MP process train as presented in Figure 4.7A and Table 4.2. However, GAC was very effective in reducing the total AOC concentration from an average of 106 µg/L, to an average of 39
to 45 µg/L (63%-58% reduction) through the control GAC contactors. Note that the total AOC concentration means of the two GAC control effluent streams were similar, 14% difference. (See Figure 4.7A and Table 4.2.) GAC adsorption following the UV/H₂O₂ process was effective in reducing the total AOC concentration from an average of 141 µg/L for LP process train, to an average of 54 µg/L (62% reduction) in the associated GAC effluent and from an average of 137 µg/L for MP process train, to an average of 45 µg/L (67% reduction) after GAC adsorption, ultimately resulting in total AOC concentrations similar to the GAC control effluent streams. (See Figure 4.7A and Table 4.2.) Overall, the removal of total AOC by GAC was very consistent regardless of whether the influent water had received UV/H₂O₂ treatment.

The quantity and type of AOC formed or reduced by the pilot unit processes differed. P17 AOC concentration was measured by the growth of Pseudomonas fluorescens. As was discussed in the introduction, the P17 organism is able to utilize various compounds to promote growth. This organism can survive using many carbon substrates as energy sources (van der Kooij et al., 1982 and AwwaRF and KIWA 1988). Spirillum strain NOX is more selective in its growth substrates. Carboxylic acids primarily promote rapid growth of the NOX organism. In treatment techniques such as ozonation where compounds not readily utilized by P17 are formed, the growth of Spirillum strain NOX is a useful indicator of AOC concentration increases. Spirillum strain NOX has been shown to represent carboxylic acids. Therefore, it was selected for studying these advanced oxidation processes. An average of 83 µg/L P17 AOC concentration, and an average of 23 µg/L NOX AOC concentration was found in the CONV pilot influent as presented in Table 4.2. Both parameter concentrations increased
through the UV/H$_2$O$_2$ reactors, but as would be anticipated, the NOX AOC concentration increased more. P17 AOC concentration increased 24% (from an average of 83 to 103 µg/L P17 AOC) through both the LP and MP reactors. (See Table 4.2.) NOX AOC concentration increased from 23 to 38 µg/L (65% increase) through the LP reactor and from 23 to 35 µg/L through the MP reactor (52% increase). The greater magnitude of the NOX AOC concentration increase was reasonable considering the findings of Sarathy et al., 2007 and 2009, i.e., the ratio of hydrophilic to hydrophobic compounds increases with UV/H$_2$O$_2$ treatment.

As was previously discussed, the control GAC effluent concentrations for total AOC were similar, but P17 AOC was better removed than NOX AOC. This result was expected because GAC was less efficient in removing hydrophilic compounds that would be represented better by NOX AOC concentration, Westerhoff et al., (2005). The NOX AOC was better removed through GAC following the UV/H$_2$O$_2$ process (47-49%) than through the control GAC column (35%) because of the increased bioactivity of the GAC caused by the UV/H$_2$O$_2$ treatment and possibly because the increased NOX AOC concentration through the reactors represented different, more adsorbable compounds than represented by the NOX AOC concentration from the CONV treated process stream as shown in Table 4.2.
Figure 4.7: AOC formation (µg/L as acetate) through the pilot - UV/H$_2$O$_2$ and photolysis alone

A) UV/H$_2$O$_2$ with CONV pilot influent

B) UV/H$_2$O$_2$ with Post-GAC pilot influent

C) Photolysis with Post-GAC pilot influent

Figure 4.7: AOC formation (µg/L as acetate) through the pilot - UV/H$_2$O$_2$ and photolysis
Table 4.2: AOC formation through the pilot - UV/H$_2$O$_2$ and Photolysis alone

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<thead>
<tr>
<th>UV/H$_2$O$_2$ with CONV pilot influent</th>
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<tr>
<td><strong>AOC µg/L as acetate</strong></td>
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<td>LP GAC</td>
<td>MP</td>
<td>MP GAC</td>
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<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

**Changes in AOC as acetate through treatment processes**

| | LP | MP | LP GAC | MP GAC | GAC | GAC |
| | Reactor | Reactor | Control | Control | #1 | #2 |
| P17 | 24% | 24% | -67% | -74% | -71% | -64% |
| NOX | 65% | 52% | -47% | -49% | -35% | -35% |
| Total | 33% | 30% | -62% | -67% | -63% | -58% |
**UV/H₂O₂ with Post-GAC pilot influent**

**AOC µg/L as acetate**

<table>
<thead>
<tr>
<th></th>
<th>Pilot</th>
<th>LP</th>
<th>MP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent</td>
<td>44</td>
<td>42</td>
<td>43</td>
</tr>
<tr>
<td>Effluent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P17 Avg.</td>
<td>64</td>
<td>73</td>
<td>73</td>
</tr>
<tr>
<td>NOX Avg.</td>
<td>20</td>
<td>31</td>
<td>30</td>
</tr>
<tr>
<td>Total Avg.</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

**Changes in AOC as acetate through treatment processes**

<table>
<thead>
<tr>
<th></th>
<th>LP</th>
<th>MP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor</td>
<td>-5%</td>
<td>-2%</td>
</tr>
<tr>
<td>P17 Avg.</td>
<td>55%</td>
<td>50%</td>
</tr>
<tr>
<td>NOX Avg.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Avg.</td>
<td>14%</td>
<td>14%</td>
</tr>
</tbody>
</table>
Photolysis with Post-GAC pilot influent

AOC µg/L as acetate

<table>
<thead>
<tr>
<th></th>
<th>Pilot Influent</th>
<th>LP Effluent</th>
<th>MP Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>P17 Avg.</td>
<td>33</td>
<td>45</td>
<td>31</td>
</tr>
<tr>
<td>NOX</td>
<td>22</td>
<td>23</td>
<td>24</td>
</tr>
<tr>
<td>Avg.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>55</td>
<td>68</td>
<td>56</td>
</tr>
<tr>
<td>Avg.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>(n)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Changes in AOC as acetate through treatment processes

<table>
<thead>
<tr>
<th></th>
<th>LP Reactor</th>
<th>MP Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>P17 Avg.</td>
<td>36%</td>
<td>-5%</td>
</tr>
<tr>
<td>NOX</td>
<td>5%</td>
<td>10%</td>
</tr>
<tr>
<td>Avg.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>24%</td>
<td>1%</td>
</tr>
<tr>
<td>Avg.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The total AOC concentration in the pilot influent was 40% lower (64 µg/L vs. 106 µg/L) when Post-GAC water was used as the pilot influent rather than CONV treated water as
presented in Figure 4.7B and Table 4.2. Because the Post-GAC pilot influent contained less UV absorbable organics, 80% atrazine reduction was obtained with less UV energy. The total AOC concentration increased slightly through the reactors during the Post-GAC influent phases, from 64 µg/L to 73 µg/L (14%) for both the LP and MP reactors. This increase in total AOC concentration was less than the 30 to 33% increase in total AOC concentration when CONV treated water was used as pilot influent. The lesser increase in total AOC concentration when Post-GAC served as pilot influent was because the TOC concentration was lower. Larger molecular weight humic compounds, potentially precursors of AOC, are well-removed by GAC (Sontheimer et al., 1988) and (Morris and Newcombe, 1993). Thus, there is a lower concentration of these humics in the Post-GAC pilot influent to act as AOC precursors. The P17 AOC concentration did not increase through the reactors when Post-GAC water was used as pilot influent. The lower concentration of organics in this process stream and the reduction of the larger molecule AOC precursors by the GAC pretreatment contributed to this result. The NOX AOC concentration increased from 20 to 30 - 31µg/L, about 50%, again indicative of carboxylic acid formation through the UV/H₂O₂ reactors as demonstrated in Table 4.2.

Three experimental pilot runs were performed using photolysis alone. However, these results were not able to be directly compared to the UV/H₂O₂ results for AOC concentration because an 80% atrazine degradation was not achievable. Also because of the aforementioned technical considerations, the LP reactor UV dose (approximately 800 mJ/cm²) was higher than the MP reactor dose (approximately 280 mJ/cm²). So no direct comparison between LP and MP technologies can be made for the photolysis study. Nevertheless, the relative increases in P17 and NOX AOC concentrations are of
interest. Photolysis using Post-GAC pilot influent created no increase in NOX AOC concentration, because without the H$_2$O$_2$, less oxidation takes place and few carboxylic acids are formed. (See Figure 4.7C and Table 4.2.) The P17 AOC concentration increased through the LP reactor, but not through the MP reactor as demonstrated in Table 4.2. This increase was likely associated with the higher LP reactor dose focused near the 254 nm wavelength. This wavelength is known to be well-absorbed by humic materials. Photolysis of the humic materials would thus proceed. As was previously discussed, the P17 AOC represents a wide variety of smaller molecular weigh assimilable compounds.

Van der Kooij (1992) recommended that unchlorinated systems maintain AOC concentrations below 10 µg/L. Even the GAC effluent samples had total AOC concentrations above this value. (See Table 4.2.) If a utility with a source water similar to GCWW’s wished to maintain a total AOC concentration less than 10 µg/L, a GAC empty bed contact time greater than the pilot condition of 15 minutes may be required. LeChevallier et al., 1990 and 1996 provided some evidence that chlorine disinfected systems may limit regrowth and coliform occurrence by maintaining AOC concentrations less than 50 to 100 µg/L. Chlorine provides some protection against regrowth. Only the UV/H$_2$O$_2$ reactor effluent streams and the CONV pilot influent samples had total AOC concentrations exceeding this range as presented in Figures 4.7 and 4.8.

4.3.3.2. Biofilm Annular Reactors after GAC Pilot Contactors

Because the pilot GAC effluent streams had such low AOC concentrations, annular biofilm reactors were employed to examine biofilm production more closely. The annular reactors were operated continuously on the undisinfected GAC effluent streams. The
experiments were begun during the most biologically active stage of GAC, i.e., near the end of the run and during warm weather conditions. The experiment ran from September 4, 2008 to October 2, 2008, which corresponded to run-day 300 to 328 of the GAC. The temperature ranged from 27 to 28°C and the TOC from 0.82 to 1.95 mg/L for this time period. The biofilm from the coupons was extracted from the reactors and analyzed by two methods: the traditional HPC method and a ATP-bioluminescence method developed internally. HPC is a microbiological parameter and tends to have more scatter in the data than a chemical parameter. Thus, a log scale was used to display the data. When analyzing biofilm by this method, one can only discern differences in magnitudes of order. Even with this caveat, the reproducibility of individual coupons was not as good as would be desired. Overall, the GAC process streams for the two controls produced similar HPCs. The HPCs of these control samples were less than those receiving water from the UV/H$_2$O$_2$ reactors. The LP reactor process stream data was the least precise. However, the coupons from this process stream tended to have slightly lower HPCs than the coupons from the MP process stream. (See Figure 4.8A.)
Figure 4.8: Biofilm formation on annular reactor coupons

A) Pilot GAC effluent – heterotrophic plate counts (HPC/mL)

B) Pilot GAC effluent – ATP measured as Relative Light Units (RLU)

Figure 4.8: Biofilm formation on annular reactor coupons
The ATP-bioluminescence method of biofilm quantification was based on the amount of ATP present. This method was dependant on viability of the organisms. Because the ATP-bioluminescence method was a chemically based analysis, and does not have the problem of cell separation, the data tend to be more precise. For this reason a linear scale can be used for the concentration axis as displayed in Figure 4.8B. However, there are still situations that can cause the test to produce outlying data points. ATP is common to all microbes and larger cells such as protozoa require more energy to thrive. Therefore, if larger cells are present, they can skew the ATP data. The data exhibited good precision, with two outlying data points, likely caused by the presence of a larger microorganism. Nevertheless, it was clear that the control GAC column effluent streams produced similar results. The GAC effluent following the LP reactor also produced results similar to the controls. The MP stream GAC effluent produced the highest results. The HPC and the ATP-bioluminescence methods showed different results because the HPC method grew the organisms in a nutrient media under ideal conditions. Injured cells had the opportunity to repair (LeChevallier et al., 1990). The ATP-bioluminescence method results represented cell viability at the time that the coupons were removed from the annular reactors and biofilm extracted. The data would suggest that the organisms produced by the MP process stream were more viable than those produced by the LP process stream, even though the HPCs for the two streams were similar. The increased viability of the biofilm produced in the MP UV reactor train is potentially a result of the multiple UV wavelengths of the MP reactor yielding different growth producing materials than the LP reactor.
4.4. Conclusions

- Some slight mineralization of TOC occurred through the UV/H\(_2\)O\(_2\) reactors. After GAC run day 220, the GAC effluent streams that had received UV/H\(_2\)O\(_2\) treatment produced 16% lower TOC concentrations than the control GAC effluent streams that had not received UV/H\(_2\)O\(_2\) pretreatment. The UV/H\(_2\)O\(_2\) pretreatment created microbially assimilable compounds, increasing the bioactivity of the organically loaded GAC. The warmer temperatures after run day 220 also increased bioactivity.

- The pilot reactors were able to consistently achieve the desired 80% atrazine degradation, allowing comparison of the LP and MP lamp technologies for by-product formation for this desired contaminant destruction. However, it is important to note that these pilot-scale reactors may give different results than optimized full-scale reactors.

- AOC concentration increased through the reactors. The degree of increase was related to the NOM concentration of the pilot influent. The total AOC concentration in the pilot influent was 40% lower when Post-GAC water was used as the pilot influent rather than CONV treated water. Larger molecular weight humic compounds, potentially precursors of AOC, are well-removed by GAC. Thus, there is a lower concentration of these humics in the Post-GAC pilot influent versus the CONV pilot influent to act as AOC precursors. Because the Post-GAC pilot influent contained less UV absorbable organics, 80% atrazine reduction was obtained with less UV energy. Therefore, the total AOC concentration increased slightly through the reactors during the Post-GAC
influent phases (14%) for both the LP and MP reactors, while the CONV pilot influent produced a 30 to 33% increase in total AOC concentration.

- The average P17 AOC concentration increased 24% through the LP and MP reactors when CONV water was used as pilot influent. The P17 AOC concentration did not increase through the reactors when Post-GAC water was used as pilot influent. As with the total AOC, the lower concentration of organics in this process stream and the reduction of the larger molecule P17 AOC precursors by the GAC pretreatment contributed to this result.

- The average NOX AOC concentration increased 65% through the LP reactor and 52% through the MP reactor (CONV pilot influent). The average NOX AOC concentration increased 55% through the LP reactor and 50% through the MP reactor when Post-GAC water was used as pilot influent, indicative of carboxylic acid formation through the UV/H₂O₂ reactors. Carboxylic acids promote the growth of the NOX organism.

- LP UV photolysis (at a dose of approximately 800 mJ/cm²) produced a 36% average P17 AOC concentration increase when using Post GAC as pilot influent. No NOX AOC concentration increase was observed, because LP UV photolysis is not an advanced oxidation process that produces carboxylic acids and other oxygenated species.

- MP UV photolysis (at a dose of approximately 280 mJ/cm²) produced no appreciable AOC concentration increase when using Post GAC as pilot influent.
This dose was not sufficient to chemically alter the NOM enough to produce AOC.

- GAC adsorption before or after the UV/H\textsubscript{2}O\textsubscript{2} process greatly reduced the resulting AOC concentration. The final product in either case contained AOC concentrations below 75 µg/L.

- Biofilms with greater HPCs were observed in the GAC effluent streams receiving UV/H\textsubscript{2}O\textsubscript{2} pretreatment. These results are consistent with the AOC results.

- The effluent streams of the GAC column proceeded by the MP UV reactor exhibited more viable biofilm than the other GAC effluent streams based on an ATP bioluminescence method. The increased viability of the biofilm produced by the MP UV reactor is likely a result of the multiple UV wavelength emissions characteristic of this technology. More research should be performed in this area.

4.5. **Acknowledgements**

We would like to acknowledge the support of KWR Watercycle Research Institute, the Dutch Ministry of Economic Affairs and the Water Research Foundation (formerly the American Water Works Research Foundation) for their support of this research. Additionally, we would like to recognize the contributions of Nick Ashbolt and Tammie Gerke of the USEPA and the efforts of the GCWW staff.

4.6. **References**

American Water Works Research Foundation Report, Denver, CO.


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Sontheimer, H., Crittenden, J.C., Summers, R.S. (1988) Activated Carbon for Water Treatment. 2nd ed., DVGW-Forschungsstelle, University of Karlsruhe, Germany, distributed in the USA by AWWA.


Chapter 5

The Effect of UV/H\textsubscript{2}O\textsubscript{2} Treatment on Disinfection byproduct Formation Potential under Simulated Distribution System Conditions
Advanced oxidation with ultraviolet light and hydrogen peroxide (UV/H₂O₂) produces hydroxyl radicals that have the potential to degrade a wide-range of organic micro-pollutants in water. Yet, when this technology is used to reduce target contaminants, natural organic matter can be altered. This study evaluated disinfection by-product (DBP) precursor formation for UV/H₂O₂ while reducing trace organic contaminants in natural water (> 90% for target pharmaceuticals, pesticides and taste and odor producing compounds and 80% atrazine degradation). A year-long UV/H₂O₂ pilot study was conducted to evaluate DBP precursor formation with varying water quality. The UV pilot reactors were operated to consistently achieve 80% atrazine degradation, allowing comparison of low pressure (LP) and medium pressure (MP) lamp technologies for DBP precursor formation. Two process waters of differing quality were used as pilot influent, i.e., before and after granular activated carbon adsorption. DBP precursors increased under most of the conditions studied. Regulated trihalomethane formation potential increased through the UV/H₂O₂ reactors from 20 to 118%, depending on temperature and water quality. When Post-GAC water served as reactor influent, less DBPs were produced in comparison to conventionally treated water. Haloacetic acid (HAA5) increased when conventionally treated water served as UV/H₂O₂ pilot influent, but only increased slightly (MP lamp) when GAC treated water served as pilot influent. No difference in 3-day simulated distribution system DBP concentration was observed between LP and MP UV reactors when 80% atrazine degradation was targeted.
5. The Effect of UV/H$_2$O$_2$ Treatment on Disinfection Byproduct Formation Potential under Simulated Distribution System Conditions

5.1. Introduction

UV/H$_2$O$_2$ advanced oxidation is a promising drinking water technology for the reduction of a broad-spectrum of synthetic organic contaminants and undesirable natural organic constituents. UV/H$_2$O$_2$ advanced oxidation combines direct photolysis and advanced oxidation through indirect photolysis for the destruction of organic compounds in water (Pereira et al., 2007). Medium pressure (MP) and low pressure (LP) UV lamps are commonly used in drinking water treatment plants. MP lamps use more electrical energy, but require less plant area. Both MP and LP lamps emit light at wavelengths that can cause hydroxyl radical formation and photolysis, however the difference in their spectrum (polychromatic versus monochromatic light respectively) may affect various chemical bonds differently, generating different degradation products. Natural organic matter (NOM) in drinking water sources is at least an order of magnitude greater in concentration than most target contaminants. As such, it is important to evaluate NOM degradates and their impact on water quality. Upon UV/H$_2$O$_2$ treatment, researchers have noted a reduction in NOM aromaticity (Thomson et al., 2004, Kleiser and Frimmel, 2000, Toor and Moseni, 2007 and Sarathy and Mohseni, 2007 and 2010), a shift to smaller molecular size (Sarathy and Mohseni, 2009), the creation of more biodegradable compounds (Thomson et al., 2004, Toor and Mohseni 2007, Sarathy and Mohseni, 2009) and a decrease in hydrophobicity (Sarathy and Mohseni, 2009 and 2010).
The use of granular activated carbon (GAC) with UV/H\textsubscript{2}O\textsubscript{2} advanced oxidation can be beneficial. GAC removes NOM, particularly the higher molecular weight and more aromatic components. When used after UV/H\textsubscript{2}O\textsubscript{2}, GAC can remove unintended degradation products and quench excess hydrogen peroxide. When used before UV/H\textsubscript{2}O\textsubscript{2}, GAC adsorption can provide reactor influent water with low NOM and UV absorbance. Lower NOM reduces the UV energy requirements and potentially leaves less NOM for unintended transformation. Also, GAC can promote biodegradation of NOM. Metz (2011) describes the effects of biodegradation with UV/H\textsubscript{2}O\textsubscript{2} under the conditions of this present study.

Free chlorine is a commonly used disinfectant in many parts of the world. Since the 1970s it has been known that disinfection by-products (DBPs) with potential health effects were formed when drinking water was chlorinated. Aquatic NOM is complex and while much research has been performed to evaluate chlorination of NOM, all reaction mechanisms during chlorination have not been elucidated. NOM is generally characterized as hydrophobic, transphilic, hydrophilic with acid, base and neutral subdivisions (Croué et al., 2006). These operationally defined fractions can provide information relative to DBP precursors. Researchers have determined that the hydrophobic/non-polar NOM accounts for the majority of DBP formation (Liang and Singer, 2003). However, Hwang et al. (2001) found that even though upon chlorination non-polar NOM generally results in more DBPs on an organic carbon basis, polar NOM can produce a significant amount of DBPs, particularly haloacetic acids. Activated aromatic species such as β-dicarbonyl compounds have also been identified as reactive DBP precursors (Dickenson, et al., 2008). Many nations have set maximum
contaminant levels (MCLs) for the sum of four trihalomethanes (THM) and the sum of five haloacetic acids (HAA5). In 2005 the World Health Organization set acute guidelines for the individual THMs emphasizing the varying toxicity of these compounds.

Numerous researchers have studied the reduction of NOM and DBP precursors through UV/H$_2$O$_2$. Matilainen and Sillanpää (2010) and Bond, et al. (2011) have published comprehensive review articles that summarize this NOM and DBP formation potential work, respectively. Some researchers have found that at lower more practical UV/H$_2$O$_2$ conditions small increases in DBP formation potential can occur (Kleiser and Frimmel, 2000, Toor and Moseni, 2007, Dotson et al., 2010 and Sarathy and Mohseni, 2010).

Although many researchers have reported that at disinfection doses UV does not increase DBP formation, Magnuson et al., (2002) found that UV direct photolysis and UV/H$_2$O$_2$ can alter extracted NOM, increasing disinfection by-product precursors. Mass spectra varied with UV dose ranging from 20 to 140 mJ/cm$^2$, indicating a change in NOM chemical structure. The change in dose also appeared to increase the reactivity of the extracted organic matter with subsequent chlorination. The magnitude of spectral changes was greater for medium pressure than low pressure lamps at equal doses.

Kleiser and Frimmel (2000) found that with short irradiation times, the UV/H$_2$O$_2$ process increased THM precursors. Toor and Moseni (2007) observed that UV/H$_2$O$_2$ was effective in reducing DBP formation potential only at UV doses >1000 mJ/cm$^2$ and at H$_2$O$_2$ doses > 23 mg/L. Saranthy and Mosheni (2010) reported that at UV doses between 500 and 2000 mJ/cm$^2$ with 15 mg/L of H$_2$O$_2$, there was a significant reduction in TOC and SUVA that was not matched by the small reductions in DBP precursors. However, when hydrophobic humic acids were reduced, improved reductions were
noted. Dotson and colleagues (2010) reported that at a UV dose of 1000 mJ/cm² and 10 mg/L H₂O₂ THM yield was increased. The researchers found that THM yield correlated with hydroxyl radical exposure.

A UV/H₂O₂ pilot-scale study was conducted to evaluate disinfection by-product precursor formation. The research was conducted over a full-year in order to cover seasonal variations and different levels of GAC breakthrough. DBP formation potential was evaluated while operating the pilot plant to meet practical performance goals. Other studies have compared LP and MP lamps for NOM transformation at equal UV doses (Dotson et al., 2010 and Magnuson et al., 2002). The objective of this study was to evaluate the impact of UV/H₂O₂ on THM and HAA5 precursor formation under UV/H₂O₂ conditions sufficient to achieve advanced oxidation performance goals (i.e., consistently reducing pharmaceutical compounds, pesticides and odor producing compounds by more than 90% and atrazine by 80%). Two plant-process sources with different natural organic composition and concentration were evaluated for UV/H₂O₂ treatment with LP and MP technologies. Disinfection by-product formation potential was investigated for each unit process in the continuous flow pilot plant, including UV/H₂O₂ reactors, GAC columns following the UV/H₂O₂ reactors, and controls for each process.

5.2. Methods

5.2.1. Facilities

The source water for the UV/H₂O₂ pilot influent was drawn from two locations within Greater Cincinnati Water Works’ (GCWW) surface water treatment plant. Location one was after coagulation, settling and filtration, i.e., conventional treatment (CONV). Location two was from combined GAC adsorber effluent (Post-GAC). Plant GAC
contact time averaged about 15-20 minutes during the study. Water entering the GAC facility had a total organic carbon (TOC) averaging 1.9 mg/L; water exiting the facility had a TOC averaging 0.9 mg/L. The GAC facility also served to significantly reduce disinfection by-product precursors. After becoming exhausted (average combined effluent of 150 days, maximum combined effluent 200 days), the GAC was thermally reactivated. A schematic of the full-scale process train, indicating these pilot influent stream locations is shown in Appendix Figure D.1.

Appendix Figure D.1 presents pertinent water quality data for GCWW plant processes that were used as the two pilot influent streams.

The CONV pilot influent water had been coagulated, flocculated and filtered which decreased the TOC concentration by 30% (from 2.5 to 1.7 mg/L), and specific ultraviolet absorbance (SUVA) from 3.4 to 2.6 L/mg-M on average, while GAC adsorption reduced the TOC concentration by 65% (from 2.5 to 0.85 mg/L) of the raw water concentration and reduced SUVA from 3.4 to 1.7 L/mg-M. The Post-GAC water was lower in total organic carbon and generally followed the seasonal trend of the CONV water. However, during the summer months GCWW reactivated the GAC more frequently to produce an average run of 108 days as compared to the annual average of approximately 150 days. The increased reactivations reduced the DBP precursors, so that even during the warmest summers the utility would be able to meet DBP regulations. Likewise, the UV$_{254}$ absorbance of the Post-GAC water exhibited very little increase in the summer, although the UV$_{254}$ absorbance of the CONV water has an increased UV$_{254}$ value in the warmer temperature months. For most of the year the Post-GAC water had significantly lower SUVA values than the CONV water. Thus, it can be assumed that the Post-GAC
water exhibited a different organic character (i.e., less aromatics and conjugated double bonds) and lower organic concentration than the CONV water. During the late winter and early Spring, however, the SUVA values of the two waters were similar. This is when the GAC is most spent, averaging about 200 run days. Figure 5.1 depicts the variability of natural organic matter in the two pilot influent waters.

**Figure 5.1:** Organic Constituents in Conventionally Treated (CONV) & Post-GAC Treated Water (2007-08)
5.2.2. Pilot Plant Design and Operation

The pilot unit was in continuous operation from October of 2007 until October 2008. It consisted of a constant head tank, the peroxide and contaminant feed systems, the UV reactors and the GAC columns. Figure 5.2 depicts the layout of the pilot including the location of the chemical injection and sampling points. CONV or Post GAC water was pumped to a constant head tank. The water flow split into two lines before entering the UV reactors. The contaminant solutions and the 8% hydrogen peroxide solution were injected through two inline injection mixers. A 10 mg/L $\text{H}_2\text{O}_2$ and a 2 µg/L atrazine concentration were targeted. The other target contaminants (See Table 3.1.) were spiked at similarly low levels. The peroxide dose was based on preliminary studies performed at KWR, the Netherlands. This peroxide dose insured that the target contaminant reductions were achieved with a reasonable UV dose.

The LP reactor (Aquionics model ALT320 TOC reduction range) consisted of eight LP lamps oriented parallel to the central axis and placed equidistantly at about a 11 cm radius from that axis. The MP reactor (Aquionics model Photon II TOC reduction range) consisted of one MP lamp oriented parallel to the flow, and could be operated at 4 power levels ranging from 75 to 100% of the power. The effluent from both UV reactors and the control water (pilot influent water before the hydrogen peroxide injection point but after the contaminant injection point) were pumped to four GAC pilot columns. Two GAC columns were fed by the control water, control columns 1 and 2. The remaining two columns received the effluent of the LP reactor and the MP reactor, respectively. The GAC columns contained reactivated GAC with an empty bed contact time of 15
minutes. For more specific details of the pilot design and construction see Chapter 4.2.2.

**Figure 5.2:** Pilot plant process schematic at GCWW

During each quarter UV/H₂O₂ was studied using CONV pilot influent water and Post-GAC pilot influent water. The operation of the system was based on performance. The UV/H₂O₂ system was operated to degrade atrazine by 80% through both the LP and MP reactor trains (effecting a degradation of greater than 90% for spiked pharmaceutical compounds, pesticides and odor producing compounds). Atrazine was chosen to calibrate the system because it was not completely destroyed under the practical UV/H₂O₂ conditions that gave excellent reduction to the other contaminants. Since the UVT₂₅₄ and TOC concentration of the water varied seasonally, the operational
conditions of the UV reactors were adjusted each quarter and during both CONV and Post-GAC pilot influent phases of the study. When the contaminant spiking phases were completed, the CONV water was used as pilot influent and the reactors were maintained at the 80% atrazine degradation operating conditions.

Additionally, several other water quality parameters, such as TOC, bromide and alkalinity were tested at various frequencies through the pilot. The analytical methods for these tests were from the Standard Methods for the Examination of Water and Wastewater (Standard Methods, 1998). (See Appendix Table D.2.)

5.2.3. Simulation of Distribution System, Chlorine Quenching and DBP Analysis

Simulated distribution system (SDS) tests were used to determine DBP formation. Water samples were held at normal plant water conditions and distribution system temperatures for three days to reflect the normal maximum detention of the drinking water distribution system. The samples were held in headspace free, organic-free amber bottles in enclosed, thermally-insulated boxes with finished plant water continually passing through the boxes. The temperature of the water varied seasonally with temperatures ranging from 6 to 29 ºC.

The amount of chlorine added depended upon whether the sample contained hydrogen peroxide. Approximately 2.09 mg of chlorine are required to quench 1 mg of hydrogen peroxide based on stoichiometry. The samples were chlorinated with 2.2 to 2.3 mg/L of chlorine per mg/L of hydrogen peroxide to produce a slight chlorine residual and then analyzed for chlorine residual. Additional chlorine was added to equal the actual RMTP chlorine dose. At the end of the 3-day period, chlorine residual was determined.
Samples not within normal plant distribution chlorine residuals (0.6 to 1.2 mg/L) were not considered.

At the completion of the 3-day SDS hold period, samples were prepared for DBP analysis. Residual chlorine was quenched as specified by the particular analytical method. Sodium thiosulfate was used to quench the chlorine for THM samples, and ammonium chloride was used to preserve the HAA samples. All samples were stored at 4 °C until they were analyzed (within two weeks). Four THMs and five HAAs were measured using USEPA method 542.2 and method 552.2, respectively. Approximately ten percent of the samples were analyzed in duplicate as a quality control check.

5.3. Results and Discussion

5.3.1. Atrazine Calibration of the pilot Plant

To achieve 80% atrazine degradation throughout the study, UV doses between 800-2000 mJ/cm² were required for the LP reactor and 200-500 mJ/cm² were required for the MP reactor with 10 mg/L hydrogen peroxide. Atrazine reduction was between 75-85% for most of the study quarters, with the only exception being the first quarter of the study when it was measured at 62% for the LP reactor. The reason for the low value during the first quarter was iron fouling, a situation that was remedied for subsequent experiments.

5.3.2. Natural Organic Matter Changes

The TOC concentration of the pilot influent water varied over the 12 month study, fluctuating between 1.2-2.6 mg/L for the CONV water and 0.6-1.0 mg/L for the Post-GAC water. (See Figure 5.1.) GAC adsorption can greatly reduce the concentration of
organic compounds, including NOM. Because the quantity of NOM is reduced and the relative composition is altered, the concentration of DBP precursors is likely reduced. Also, as was mentioned previously, the pilot process included GAC pilot columns after the reactors when CONV water was used as pilot influent. So, GAC adsorption had the potential of reducing DBP precursors, before or after the UV/H$_2$O$_2$ reactors depending on the pilot influent.

Figure 5.3 represents TOC concentration through the pilot plant, including the effluent of the GAC pilot columns when CONV water was used as the pilot influent. The top three curves depict CONV influent TOC concentration and the two UV/H$_2$O$_2$ reactor effluent TOC values. Westerhoff et al., (1999) found that different methods used to determine the reactivity of NOM to the hydroxyl radical tend to yield similar reactivities for isolated NOM or natural waters and the magnitude of these hydroxyl radical reactivities fell within a narrow range, $2.6 \times 10^8$ to $4.5 \times 10^8$ L M(C)$^{-1}$s$^{-1}$. He later refined these constants through direct measurement $1 \times 10^8$ to $5 \times 10^8$ L M(C)$^{-1}$s$^{-1}$ (Westerhoff et al., 2007). Hydroxyl radicals generated by the UV/H$_2$O$_2$ process reacted with the natural organic matter, but only a small percentage of NOM mineralization was achieved at 80% atrazine degradation (Metz et al., 2011).

The bottom four curves represent TOC concentrations for the GAC column effluent streams from the LP and MP reactor process trains and the two control GAC columns. (See Figure 5.3.) Typical breakthrough curves were observed for all four GAC pilot column effluent streams. TOC concentration in the GAC effluent streams ranged from 0.2 to 1.6 mg/L over the study period. At the beginning of the GAC pilot column runs, there was excellent TOC removal, and over the first 140 to 150 days as the GAC
became loaded with organics, the effluent TOC concentration exhibited a rising trend, even though the influent TOC concentration was declining. After this point, the GAC effluent TOC concentrations reflected the increases and decreases of the TOC concentration in the GAC influent. However, some TOC removal was observed through all GAC columns during the study period. By run day 220 there was a clear separation in the TOC concentrations of the GAC effluent streams that had received UV/H₂O₂ pretreatment and those that had not, as shown in Figure 5.3. Overall, the GAC effluent following the UV/H₂O₂ reactors resulted in 8% less TOC concentration than the control GAC effluent streams. After GAC run day 220, the GAC effluent following the UV/H₂O₂ reactors averaged 16% less TOC concentration than the GAC effluent of the control process streams. Metz et al., (2011) describes the bioactivity of the GAC columns and the biofilm potential differences in the experimental and control process streams.
The character of the NOM was altered through UV/H$_2$O$_2$ as indicated by the decline in SUVA through the UV/H$_2$O$_2$ reactors. (See Figure 5.4.) When the CONV water was used as pilot influent, SUVA was reduced on average through the reactors from 2.6 L/mg-M to 2.3 L/mg-M (MP) and 2.2 L/mg-M (LP) and to 1.8 L/mg-M in the control GAC columns. The CONV water that was UV/H$_2$O$_2$ treated and subsequently GAC treated had the lowest SUVA values, averaging 1.4 L/mg-M. (See Figure 5.4A.)

During the CONV water phase, the GAC pilot columns following the reactors preferentially removed UV$_{254}$ absorbable organics (aromatics and unsaturated chromophores), thus reducing SUVA. At study conditions, UV$_{254}$ absorbance and SUVA were reduced through the reactors due to the transformation of aromatic groups and
conjugated double bond molecules of the NOM. Saranthy and Mohseni (2007) (2009), Thomson, el al. (2004), Kleiser and Frimmel (2000), Toor and Mosheni (2007) and (Gallard and Von Gunten, 2002a and 2002b) noted a reduction of aromaticity of NOM with UV/H$_2$O$_2$ treatment. Sarathy and Mohseni 2007 reported that under advanced oxidation conditions typically applied at drinking water facilities, NOM was not mineralized but was partially oxidized resulting in significant reduction of aromaticity as measured by high performance size exclusion chromatography. Their findings agree with the SUVA results from this present research.

In conventional treatment processes SUVA has been shown to correlate well with “activated” aromatic structures for specific waters (aromatic sites substituted with oxygen- and nitrogen-containing functional groups, i.e., phenolics and aromatic amines) that constitute the primary sites attacked by chlorine or other oxidants (Norwood et al., 1980; Reckhow et al., 1990, Westerhoff et al., 1999). Even though SUVA can be a relative indicator of DBP formation potential through conventional physical treatment processes, it cannot be assumed that chemical alteration by advanced oxidation would result in the reduction of DBP formation potential. In fact, chemical alteration by UV/H$_2$O$_2$ has the potential to cause the formation of new DBP precursors (Sarathy and Mohseni, 2010, Dotson et al., 2010, Toor and Moseni 2007, Magnuson et al. 2002 and Kleiser and Frimmel, 2000).

When Post-GAC water was used as pilot influent, no reduction in SUVA was observed through the reactors. (See Figure 5.4B.) The Post-GAC pilot influent was consistently lower (slightly) in SUVA than the reactor effluent streams. This is because much of the UV$_{254}$ absorbable organic materials (aromatics and conjugated double bonds) and NOM
of higher molecular weight were removed through the GAC adsorption process and was not available for transformation by UV/H₂O₂. (See Figure 5.1) This data suggests that the Post-GAC NOM reacted differently to the UV/H₂O₂ treatment than the CONV NOM. Although, it is important not to conclude too much from this low organic water with TOC and UV₂₅⁴ values approaching the analytical detection limits.

![Figure 5.4: SUVA through Pilot Plant 5A with CONV pilot Influent; 5B with Post-GAC Pilot Influent](image-url)
5.3.3. Trihalomethane Formation

5.3.3.1. Preliminary Trihalomethane Formation Studies

Liu et al., (2003) recommended the use of 0.1 mg/mL catalase to quench the hydrogen peroxide dose because it does not require multiple measurements of chlorine and peroxide residuals. However, this would not be a feasible approach for drinking water plants. It is expected that most plants would use chlorine or GAC to quench the hydrogen peroxide. For those pilot plant samples that did not pass through GAC after \( H_2O_2 \) addition, chlorine was used to quench the \( H_2O_2 \). In order to investigate the effect of quenching hydrogen peroxide by chlorine pilot tests were performed. As described previously, excess hydrogen peroxide was quenched by chlorine in the SDS samples, and additional chlorine was added to achieve plant chlorine doses. Samples taken before \( H_2O_2 \) addition were dosed at typical plant chlorine doses. Chlorine doses in the SDS samples were sufficient to maintain normal distribution system chlorine residual after three days following the chlorine quenching of \( H_2O_2 \). In order to determine the effect of \( H_2O_2 \) addition and chlorine quenching of \( H_2O_2 \) residuals, TTHM 3-day SDS concentration was monitored before and after \( H_2O_2 \) addition (before UV exposure) in the pilot influent water. As can be seen in Figure 5.5, no differences in TTHM 3-day SDS concentration were observed in pilot influent before or after \( H_2O_2 \) addition, suggesting that \( H_2O_2 \) alone does not transform NOM under the conditions studied. Even though chlorine doses of greater than 20 mg/L were used to quench the 10 mg/L \( H_2O_2 \) in the post \( H_2O_2 \) samples and less than 2 mg/L chlorine were used in the samples without \( H_2O_2 \), no appreciable differences in 3-day SDS THM concentrations were observed.
Figure 5.5: Effect of hydrogen peroxide and chlorine quenching on 3-day simulated distribution system (SDS) TTHM

5.3.3.2. Total Trihalomethane Formation with Conventionally Treated Pilot Influent

During the time period that the CONV water served as the pilot influent, TTHM 3-day SDS samples were collected after 100 GAC run days. Large increases in TTHM 3-day SDS concentrations were observed through the UV/H₂O₂ reactors under study conditions. The TTHM 3-day SDS concentrations increased through both the MP and LP reactors similarly. (See Figure 5.6.) TTHM formation was controlled in large part by temperature. In April and September the UV₂₅⁴ absorbance of CONV pilot influent water was 0.03-0.04 /cm, but the temperature in April was approximately 12°C versus 24°C in September. The CONV water formed 43 µg TTHM/mg of TOC after the three day hold
in April, but 77 µg TTHM/mg of TOC in September. The reactor effluents formed 73 µg TTHM/mg of TOC in April versus 95 µg TTHM/mg of TOC in September on average. The average percent increase in µg TTHM/mg of TOC through the reactors was greater in the Spring, 69% increase versus the Fall, 23%. All GAC effluents receiving CONV pilot influent, including the controls, produced similar TTHM 3-day SDS concentrations that were considerably lower in concentration. As was noted previously, an 8% improvement in TOC reduction (average) and 16% improvement in TOC reduction (during the summer months) was observed through the GAC columns receiving UV/H₂O₂ treated water, but no corresponding reduction in TTHM 3-day SDS was observed. (See Figure 5.6.)
Figure 5.6: TTHM 3-day Simulated Distribution System (SDS) – Through UV/H$_2$O$_2$ reactors and pilot GAC columns with CONV Pilot Influent

5.3.3.3. **Total Trihalomethane Formation with Post-GAC Pilot Influent**

When the Post-GAC process stream served as the influent to the UV/H$_2$O$_2$ reactors, there was some increase in TTHM 3-day SDS concentrations, and this increase in TTHM 3-day SDS concentrations was observed through both MP and LP reactors. (See Figure 5.7.) As can be seen in Figure 5.1, less natural organic matter was present in the influent to the reactors. Not only was the TOC concentration and UV$_{254}$ absorbable materials of the Post-GAC pilot influent lower than the CONV water, but SUVA was lower. (See Figure 5.1.) Figure 5.4 illustrates that the SUVA of the Post-GAC water is less significantly altered through the reactors compared to the SUVA of the CONV
treated water. The GAC treatment removed much of the NOM, thus decreasing THM precursors. Westerhoff et al. (1999) noted a strong correlation between hydroxyl radical reactivity with NOM and SUVA. In April and September the $\text{UV}_{254}$ absorbance of Post-GAC pilot influent water was 0.01-0.02 /cm. The Post-GAC water formed 29 $\mu$g TTHM/mg of TOC in April, but 63 $\mu$g TTHM/mg of TOC in September. The reactor effluents formed 54 $\mu$g TTHM/mg of TOC in April versus 96 $\mu$g TTHM/mg of TOC in September, illustrating the effect of temperature on TTHM formation, i.e., the higher formation in September was due to the higher temperatures. The formation of TTHM/mg/L of TOC in the chlorinated reactor effluent water in September was very similar to the reactor effluent water when CONV treated water was used as pilot influent, but the April reactor effluent data using the Post-GAC pilot influent was lower than the comparable data when CONV water was used as pilot influent. The percent increase in $\mu$g TTHM/mg of TOC through the reactors, however, was greater in the Spring, 86% increase versus the Fall, 53%.
Figure 5.7: TTHM 3-day Simulated Distribution System (SDS) – Through Reactors with Post-GAC Pilot Influent

Four research groups have published results using UV/H$_2$O$_2$ conditions similar to this present study, Kleiser and Frimmel (2000), Toor and Mohseni (2007), Dotson et al. (2010) and Saranth and Mohseni (2010). Kleiser and Frimmel (2000) found that the maximum TTHM formation potential was 20% higher after UV/H$_2$O$_2$ treatment than in the control sample when held for 48 hours. After extremely high levels of irradiation, that produced greater than 10% mineralization, Kleiser and Frimmel (2000) observed that THMs began to decrease. The authors speculated that the reactions of peroxyl-radicals among themselves can lead to the production of ketones or aldehydes (in incomplete mineralization) with short irradiation times. In this present study 2-3% mineralization
was observed through the reactors when CONV treated water served as pilot influent and 4-7% mineralization was observed through the reactors when Post-GAC water served as pilot influent, Metz et al., (2011).

Toor and Mohseni (2007) observed modest increases in TTHM formation potential between 0 to 1000 mJ/cm² when 4 mg/L H₂O₂ was used. Saranthy and Mohseni (2010) observed that for UV/H₂O₂, UV doses below 1500 mJ/cm² did not reduce TTHM formation. However, no increase in TTHM concentration was observed below this UV dose with 15 mg/L H₂O₂. The natural water utilized for these tests was a reservoir water of different water quality. The natural water used by Kleiser and Frimmel (2000), Dotson et al., 2010 and this present study was from a river water source. Saranthy and Mohseni (2010) also observed greater mineralization and less DBP formation when the higher molecular weight NOM was removed. This data partially agrees with the present study. More mineralization occurred in the GAC treated water and less THMs were formed. However, the yield per µg TTHM/mg was actually slightly higher when Post-GAC water served as UV/H₂O₂ influent. The results of Dotson and colleagues (2010) agree more closely with this present study. They reported that at a UV dose of 1000 mJ/cm² and 10 mg/L H₂O₂, trihalomethane yield was increased by 21-29 µg/mg of TOC, using conventionally treated water (after chlorination and a 24 hour hold at room temperature conditions), while increasing 18-33 µg/mg of TOC when using GAC treated water. The researchers found that THM yield correlated with hydroxyl radical exposure. Hydroxylation of aromatics or the transformation of less chlorine reactive hydrophobic fraction of NOM into the more highly reactive hydrophilic NOM was believed to occur. However, the degree to which TTHM formation potential was increased depended upon
the dose of UV and H$_2$O$_2$ and the constituents in the water. Partial oxidation of NOM can lead to ring opening of aromatic structures, cleavage of conjugated double bonded carbon structures, and reduction in the degree of aromatic substitution. Ring cleavage can create more reactive sites. Hydroxyl radicals formed by the UV/H$_2$O$_2$ process may preferentially react with hydrophobic fractions of NOM yielding hydrophilic products (Sarathy and Mohseni 2009 and 2010). Hwang et al. (2001) found that polar NOM can produce a significant amount of DBPs.

If the reactor effluent water from the CONV process stream were to be delivered directly to the distribution system, the system would not meet U.S. TTHM regulations. After GAC adsorption, pilot effluents (with and without UV/H$_2$O$_2$) produced similar THM 3-day SDS concentrations which would meet these regulations. When using Post-GAC pilot influent, the UV/H$_2$O$_2$ reactors increased the 3-day SDS TTHM concentrations. However, even after UV/H$_2$O$_2$, the reactor effluents would meet U.S. TTHM regulations.

5.3.3.4. Brominated THM Formation

When CONV treated water was used as pilot influent, the bromodichloromethane (CHBrCl$_2$) 3-day SDS concentrations varied seasonally in the influent, but there was little difference in concentration of CHBrCl$_2$ 3-day SDS concentration through the pilot reactors. The CHBrCl$_2$ 3-day SDS concentration of the CONV pilot influent water was 30 µg/L and 36 and 35 µg/L for the LP and MP reactor effluent average values, respectively. (See Table 5.1.) This is interesting considering the increase in the TTHM SDS through the reactors. The CHBrCl$_2$ 3-day SDS concentration accounted for a lesser percentage of the TTHM SDS concentration in the reactor effluent water (24% for LP effluent and 25% for MP effluent) than in the CONV pilot influent (31%) on a µg/L
basis. On a molar basis the percentages were 24, 20 and 21%, respectively. In the
effluent of the GAC columns, the CHBrCl\(_2\) 3-day SDS concentration was lower, 17 µg/L
for the GAC effluents following the reactors and 16 µg/L for the GAC effluent from the
control columns. CHBrCl\(_2\) SDS comprised 30% the TTHM SDS concentration for all
GAC column effluent water and 31% of the CONV influent. The results for CHBrCl\(_2\) are
significant because it is considered the most toxic of the TTHMs. The CHBrCl\(_2\) 3-day
SDS average concentration of the CONV influent and the associated reactor effluent
waters were above 20 µg/L, a level of concern based on some prenatal toxicological
research (Dodds and King, 2001). However, a large, well-designed study (Savitz et al.,
2005) did not deem these levels of toxicological concern.

Table 5.1: Speciation of TTHM SDS by µg/L and mmol/L

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<th>% of TTHM by conc.</th>
<th>Avg. conc. µmol/L</th>
<th>Molar % of TTHM</th>
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</tr>
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<td>Avg. conc. µmol/L</td>
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Bromoform 3-day SDS concentrations were very low ranging from an average of 2.4 to 6.0 µg/L for all sample points through the pilot plant when CONV treated water was used as pilot influent. On average 2.9% of the TTHM 3-day SDS concentration of the CONV treated water was comprised of bromoform, while the bromoform comprised 1.6% and 9 to 11% of the TTHM 3-day SDS concentration for the UV/H₂O₂ reactor effluents and the subsequent GAC column effluent waters, respectively. (See Table 5.1.) Dibromochloromethane (CHBr₂Cl) SDS concentrations ranged from an average of 18 to 21 µg/L for all sample points. Approximately 19% of the TTHM 3-day SDS concentration of the CONV treated water was comprised of CHBr₂Cl. Thirteen to 14% of the TTHM 3-day SDS concentration of the UV/H₂O₂ reactor effluent water was comprised of CHBr₂Cl and 36 to 38% in the subsequent GAC column effluent waters. (See Table 5.1.)

When Post-GAC treated water was used as pilot influent, the CHBrCl₂ 3-day SDS concentration showed a slight increase through the reactors. However, concentrations were lower than those of the CONV pilot followed by GAC adsorbers and showed less seasonal variation, averaging 6.9 µg/L in the Post-GAC pilot influent and 13 µg/L in the LP effluent and 11 µg/L in the MP effluent. (See Table 5.1.) The CHBrCl₂ 3-day SDS

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<td>-</td>
</tr>
<tr>
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<td>-</td>
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<td>-</td>
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<td>LP Effluent</td>
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<td>0.37</td>
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concentration accounted for a similar percentage of the TTHM SDS concentration in the Post-GAC pilot influent (24%) as in the reactor effluent water, 22% in the MP reactor effluent and 25% in LP reactor effluent. On a molar basis the percentages were 22% in the Post-GAC pilot influent and in the LP reactor effluent and 19% in the MP reactor effluent. (See Table 5.1.)

When using Post-GAC water as pilot influent, bromoform 3-day SDS concentrations were low, ranging from an average of 10 to 13 µg/L for all sample points. Approximately 34% of the TTHM 3-day SDS concentration of the Post-GAC treated water was comprised of bromoform, while 23 to 26% of the TTHM 3-day SDS concentration of the UV/H₂O₂ reactor effluent water was comprised of bromoform. (See Table 5.1.) Dibromochloromethane (CHBr₂Cl) 3-day SDS concentrations ranged from an average of 10 to 17 µg/L for all sample points. Approximately 33% of the TTHM 3-day SDS concentration of the Post-GAC treated water was comprised of CHBr₂Cl. Twenty-eight to 33% of the TTHM 3-day SDS concentration of the UV/H₂O₂ reactor effluent water was comprised of CHBr₂Cl. (See Table 5.1.)

Dotson (2010) found that bromide incorporation decreased after UV/H₂O₂ treatment in both CONV treated and Post-GAC waters, but it decreased more in the Post-GAC samples. This agrees with the present study. When CONV water was used as pilot influent, the percentage of TTHM as chloroform increased from 63 to 70% on a molar basis, while bromoform decreased from 1.4 to 0.9% of TTHM. When Post-GAC water was used as pilot influent, the percentage of TTHM as chloroform increased from 32 to 45% on a molar basis, while bromoform decreased from 21 to 14% of TTHM. When the
CONV treated UV/H$_2$O$_2$ reactor effluent was GAC filtered, this trend reversed. (See Table 5.1.)

The concentration of some brominated DBPs can increase after GAC adsorption and subsequent chlorination (Symons et al., 1993). Bromide is passed conservatively through the GAC and results in higher bromide to NOM ratios than in the pre-GAC water (Owen et al., 1995). So it is not surprising that the Post-GAC pilot influent had higher bromoform 3-day SDS concentrations than the CONV pilot influent. Low-aromatic components of NOM have higher bromine incorporation when chlorinated (Kitis, 2001). As was previously mentioned, the GAC treated waters in this study had lower SUVA values than the CONV treated waters, indicating less aromatic composition. It should be noted that the final 3-day SDS bromoform concentration in the final step of both treatment processes (Post-GAC pilot influent after the reactors and CONV pilot influent after reactors and GAC treatment) was 12.5 and 5.5 mg/L, respectively. These differences are not of practical concern. None of the individual THM species had 3-day SDS concentrations that exceeded the World Health Organization guidelines.

5.3.4. Haloacetic Acid Formation

HAA5 3-day SDS concentration increased through the UV/H$_2$O$_2$ MP and LP reactors when CONV water was used as pilot influent (See Figure 5.8.). The CONV pilot influent HAA5 3-day SDS concentration averaged 34 µg/L, while the LP reactor averaged 53 µg/L and the MP reactor averaged 51 µg/L. All pilot GAC effluent streams averaged 15 to 20 µg/L. HAA5 3-day SDS concentration increased slightly through the MP reactor when Post-GAC was used as pilot influent (from 14 µg/L to 20 µg/L), but did not
increase through the LP reactor. (See Figure 5.9.) All process streams (with and without UV/H₂O₂) would meet U.S. HAA5 regulations based on these results.

This present study agreed with the findings of Toor and Mohseni (2007). An increase in HAA formation potential was observed between 0-1000 mJ/cm² for 4 and 23 mg/l H₂O₂. The results of both studies differ from Saranthy and Mohseni (2010) who showed a decrease in HAA formation potential at a UV dose of 500 mJ/cm² and a H₂O₂ dose of 15 mg/L. (in contrast to 10 mg/l in this present study). The results also differ from Dotson et al., 2010 who found increases and decreases in HAA formation potential, but no discernable trend.

The increase in HAA5 precursors may be the result of the UV/H₂O₂ reaction increasing the concentration of oxygenated NOM, creating more hydrophilic compounds. Sarathy and Mohseni (2009 and 2010) reported that UV/H₂O₂ preferentially reacted with the hydrophobic fractions of NOM leading to the formation of hydrophilic products. Hwang et al., (2001) found that the hydrophilic/polar portions of NOM readily formed HAA5s upon chlorination. Apparently, the GAC treatment in this present study removed a significant portion of the NOM with the potential of forming HAA5 precursors upon UV/H₂O₂ treatment. Sarathy and Mohseni (2009 and 2010) found that when the very hydrophobic fraction of NOM was removed before UV/H₂O₂ treatment, HAA formation was reduced. In this present study GAC reduced the very hydrophobic fraction of the NOM, producing similar results.

No measurable differences between the mono-halogenated, di-halogenated and tri-halogenated species was observed for this present study. Small increases were seen in all species. This lack of differences in speciation upon UV/H₂O₂ treatment was unlike
the THM results, but agrees with the work of Dotson et al., (2010). He found that the yield of the di-halogenated and tri-halogenated species did not depend on the concentration of $\text{H}_2\text{O}_2$, but on MP dose. Reckhow (1990) noted the varying nature of dichloroacetic acid and trichloroacetic acid precursors. Increases in dichloroacetic acid were linked to the formation of diketones and aldehydes. Unlike this present study, Toor and Mohseni (2007) found that dichloroacetic acid formation increased with increasing UV doses, while trichloroacetic acid formation decreased. However, different source waters may account for the differences in the formation of species.

![Graph](image.png)

**Figure 5.8:** HAA5 3-day Simulated Distribution System (SDS) with CONV Pilot Influent
Figure 5.9: HAA5 3-day Simulated Distribution System (SDS) with Post-GAC Pilot Influent

5.4. Conclusions

For a typical river source at practical UV/H$_2$O$_2$ treatment conditions (effecting a 2-7% mineralization of NOM), the following could be concluded:

- Three-day SDS TTHMs significantly increased for both the CONV treated water and the Post-GAC reactor influent waters, creating regulatory concerns.
- Three-day SDS HAAs significantly increased for the CONV treated water and slightly increased for the Post-GAC reactor influent waters (MP lamp).
• Although increases in 3-day SDS TTHM consistently occurred through the UV/H₂O₂ reactors, the degree of increase was most affected by distribution system temperature.

• When MP and LP pilot units were operated to produce 80 percent atrazine destruction by UV/H₂O₂, the 3-day simulated distribution TTHM concentrations from both reactors were very similar year-round.

• GAC adsorption was beneficial in reducing DBP precursors whether it was employed before or after the UV/H₂O₂ reactors, although typical shifts to the more brominated THM species were observed.

• Designers of UV/H₂O₂ installations need to consider doses of UV and H₂O₂ that will minimize DBP precursors as well as reduce target contaminants to desired levels.

5.5. Acknowledgements

Various aspects of this research were conducted in cooperation with KWR Watercycle Research institute, Dunea Water, the University of Colorado, the University of Cincinnati and Philips Lighting. We would like to acknowledge the support of the Dutch Ministry of Economic Affairs and the Water Research Foundation (formerly the American Water Works Research Foundation) for their support of this research. Additionally, we would like to thank Kimberley Curry, Niranjan Selar, Katherine Jamriska, Cheri Woody and the laboratory staff of the Greater Cincinnati Water Works.
5.6. References


Chapter 6

Conclusions and Recommendations for Future Work
6. Conclusions and Recommendations for Future Work

6.1. General Conclusions

- UV/H$_2$O$_2$ can be used with GAC for excellent contaminant removal with minimal adverse effects.

- Higher NOM resulted in a higher $E_{EO}$ for UV/H$_2$O$_2$ target contaminant destruction. The $E_{EO}$ ratios between the CONV and Post-GAC water range between 1.5 and 2.0 (LP) 1.2 to 1.6 (MP) for the seven compounds studied. Higher NOM increased the $E_{EO}$ similarly for these compounds.

- Water through the UV/H$_2$O$_2$ process exhibited a change in UV absorbance from 240 to 300 nm, with the reactor effluent having less absorbance than the influent at all wavelengths. The CONV water had a more consistent percentage change, even though the overall absorbance was higher. The Post-GAC water exhibited a wider range of change. The pilot influent that represented newly reactivated GAC, exhibited the greatest change in NOM, suggesting that the GAC non-adsorbable fraction of NOM was the most reactive relative to aromatic destruction or fragmentation.

- MTBE destruction by UV/H$_2$O$_2$ correlated very well with SUVA values, indicating the importance of the type of NOM.

- $E_{EO}$ for the destruction of MTBE also correlated well with SUVA values for both the pilot-scale and bench-scale experiments

- Second order NOM reaction rate for the CONV and Post-GAC calculated using the AdOx™ model was $1.0 \times 10^8$ M$^{-1}$s$^{-1}$. The second order NOM reaction rate for
the very low NOM RO water was $1.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ for MTBE destruction, suggesting that the lower molecular weight NOM passing the membrane was more reactive than the CONV and Post-GAC waters at the time they were sampled.

- Some slight mineralization of TOC occurred through the UV/H$_2$O$_2$ reactors. After GAC run day 220, the GAC effluent streams that had received UV/H$_2$O$_2$ treatment produced 16% lower TOC concentrations than the control GAC effluent streams that had not received UV/H$_2$O$_2$ pretreatment. The UV/H$_2$O$_2$ pretreatment created microbially assimilable compounds, increasing the bioactivity of the organically loaded GAC. The warmer temperatures after run day 220 also increased bioactivity.

- The pilot reactors were able to consistently achieve the desired 80% atrazine degradation, allowing comparison of the LP and MP lamp technologies for by-product formation for this desired contaminant destruction. However, it is important to note that these pilot-scale reactors may give different results than optimized full-scale reactors.

- AOC concentration increased through the reactors. The degree of increase was related to the NOM concentration of the pilot influent. The total AOC concentration in the pilot influent was 40% lower when Post-GAC water was used as the pilot influent rather than CONV treated water. Larger molecular weight humic compounds, potentially precursors of AOC, are well-removed by GAC. Thus, there was a lower concentration of these humics in the Post-GAC pilot influent versus the CONV pilot influent to act as AOC precursors. Because
the Post-GAC pilot influent contained less UV absorbable organics, 80% atrazine reduction was obtained with less UV energy. Therefore, the total AOC concentration increased slightly through the reactors during the Post-GAC influent phases (14%) for both the LP and MP reactors, while the CONV pilot influent produced a 30 to 33% increase in total AOC concentration.

- The average P17 AOC concentration increased 24% through the LP and MP reactors when CONV water was used as pilot influent. The P17 AOC concentration did not increase through the reactors when Post-GAC water was used as pilot influent. As with the total AOC, the lower concentration of organics in this process stream and the reduction of the larger molecule P17 AOC precursors by the GAC pretreatment contributed to this result.

- The average NOX AOC concentration increased 65% through the LP reactor and 52% through the MP reactor (CONV pilot influent). The average NOX AOC concentration increased 55% through the LP reactor and 50% through the MP reactor when Post-GAC water was used as pilot influent, indicative of carboxylic acid formation through the UV/H₂O₂ reactors. Carboxylic acids promote the growth of the NOX organism.

- LP UV photolysis (at a dose of approximately 800 mJ/cm²) produced a 36% average P17 AOC concentration increase when using Post GAC as pilot influent. No NOX AOC concentration increase was observed, because LP UV photolysis is not an advanced oxidation process that produces carboxylic acids and other oxygenated species.
• MP UV photolysis (at a dose of approximately 280 mJ/cm²) produced no appreciable AOC concentration increase when using Post GAC as pilot influent. This dose was not sufficient to chemically alter the NOM enough to produce AOC.

• GAC adsorption before or after the UV/H₂O₂ process greatly reduced the resulting AOC concentration. The final product in either case contained AOC concentrations below 75 µg/L.

• Biofilms with greater HPCs were observed in the GAC effluent steams receiving UV/H₂O₂ pretreatment. These results are consistent with the AOC results.

• The effluent streams of the GAC column preceded by the MP UV reactor exhibited more viable biofilm than the other GAC effluent streams based on an ATP bioluminescence method. The increased viability of the biofilm produced by the MP UV reactor is likely a result of the multiple UV wavelength emissions characteristic of this technology.

• Three-day SDS TTHMs significantly increased for both the CONV treated water and the Post-GAC reactor influent waters, creating regulatory concerns.

• Three-day SDS HAAs significantly increased for the CONV treated water and slightly increased for the Post-GAC reactor influent waters (MP lamp).

• Although increases in 3-day SDS TTHM consistently occurred through the UV/H₂O₂ reactors, the degree of increase was most affected by distribution system temperature.
• When MP and LP pilot units were operated to produce 80 percent atrazine destruction by UV/H\textsubscript{2}O\textsubscript{2}, the 3-day simulated distribution TTHM concentrations from both reactors were very similar year-round.

• GAC adsorption was beneficial in reducing DBP precursors whether it was employed before or after the UV/H\textsubscript{2}O\textsubscript{2} reactors, although typical shifts to the more brominated THM species were observed.

• Designers of UV/H\textsubscript{2}O\textsubscript{2} installations need to consider doses of UV and H\textsubscript{2}O\textsubscript{2} that will minimize DBP precursors as well as reduce target contaminants to desired levels.

6.2. Recommendations for Future Work

• Further work is needed to better understand the chemical changes that occur with NOM upon UV/H\textsubscript{2}O\textsubscript{2} treatment. This understanding will help researchers find ways to avoid the unintended consequences of these reactions and develop technologies to deal with the problems. The fluorescence excitation-emission matrices (F-EEM) coupled with various data analysis software has been used to separate F-EEM data into protein and humic components. I believe that fractionation beforehand will improve the method even further. By looking at fractionated scans before and after various UV/H\textsubscript{2}O\textsubscript{2} treatment scenarios, a much better understanding of the changes to NOM chemistry can be gained.

• Additional work should be performed to enhance biologically active carbon after UV/H\textsubscript{2}O\textsubscript{2}. Optimizing the removal potential of the GAC should make the combined process even more viable. Recent investigations into nutrient
supplementation into biological filter influent stream have shown promise, and this approach may greatly improve the potential of GAC to remove by-products.

- Further work should be also done with biofilm annular reactors using the new ATP methodologies. Multiple repetitions of the MP vs. LP lamp results would verify subtle differences in biofilm production. Particularly in the warmer climates, these differences could be significant. This process has great promise in warmer drier areas where water is scarce and water reuse is practiced. However, the potential for biofilm formation can also be greater in these areas.

- Further study should be done on differences in the way various wave lengths of the medium pressure lamp react with NOM. The medium pressure technology significantly reduces the required footprint of the UV/H₂O₂ installation, so many systems may choose this technology. Therefore, it is important to know how each of the MP wavelengths impact NOM.

- Work needs to continue on building more efficient UV lamps or developing practical catalytic solutions that will reduce the energy use and carbon footprint of this technology.
Appendix A

Pilot Plant Operating and Background Data

Photolysis Results
Pilot Plant Operating and Background Data Photolysis Results

A.1 Pilot Plant Design

GCWW’s pilot plant consisted of a constant head tank, the peroxide and contaminant feed systems, the UV reactors, the GAC column skids, and the annular reactors. Figure A.1 shows the layout of the pilot including the location of the chemical injection and sampling points. Figure A.2 (a)-(c) are photographs of the pilot plant.

CONV or Post GAC water was pumped by 1.5 HP iron-cast centrifugal pumps into the 600 L (160 gal) polyethylene constant head tank. The constant head tank was located about 6 m (20 ft) above the UV reactors to provide sufficient head for the water flow through the unit. The total water flow was measured by a magnetic flow meter located in the main line before the first injection point. At the end of the main line the water flow split into two lines and after a flow control valve and a magnetic flow meter, it entered each of the UV reactors.

The contaminant solution and the 8% hydrogen peroxide solution were injected into two PVC online injection mixers located 0.9 m (3 ft) apart in the main line to ensure complete mixing. The contaminant solution was pumped from a polypropylene 19 or 115 L (5 gal or 30 gal) tank through a diaphragm pump into the online mixer. The hydrogen peroxide was purchased at 35% (FMC Oxypure) in 210 L (55 gal) drums, and it was diluted down to 8% on a regular basis into 115 and 230 L (30 and 60 gal) day tanks. It was fed constantly in the second mixer through a positive displacement pump. A 2 µg/L atrazine concentration and a 10 mg/L H₂O₂ concentration were targeted.
The medium pressure (MP) reactor was purchased from Aquionics (Hanovia model Photon II TOC reduction range), consisted of one MP lamp oriented parallel to the flow, and could be operated at 4 power levels ranging from 75 to 100% of the power. The reactor’s internal diameter was about 15 cm and its chamber length was approximately 97 cm. The 3.5 kW MP lamp and sleeve were Super TOC models from Aquionics with an expected lifetime for the lamp of 8,000 hours. The reactor also included an immersed pre-calibrated UV monitor (Hanovia) sensitive to UVC wavelengths, and a manual rubber wiper. A digital display on the power supply box indicated the UV intensity, UV dose, run hours, and temperature, and allowed for flow and UVT₂₅₄ input for the computation of the UV dose. The flow range through the reactor could vary between 1.8 to 10 m³/h (8 and 44 gpm).

The low pressure (LP) reactor was also purchased from Aquionics (Hanovia model ALT320 TOC reduction range), and consisted of eight LP lamps oriented parallel to the central axis and placed equidistantly at about a 11 cm radius from that axis. The reactor’s diameter was about 31 cm and its chamber length was approximately 97 cm. The 80 W LP lamps and sleeves were standard disinfection models from Aquionics with an expected lifetime for the lamps of 12,000 hours. The reactor also included an immersed pre-calibrated UV monitor (Hanovia) sensitive to UVC wavelengths, and no wipers. A display on the power supply box indicated the UV intensity, run hours, and on/off lamps. The flow range through the reactor could vary between 1.8 to 10 m³/hr (8 to 44 gpm).

The effluent from both UV reactors, as well as pilot influent water before the hydrogen peroxide injection point were pumped to four GAC pilot columns. The two GAC columns
fed by the influent water before the addition of peroxide, and after the injection of contaminants, were the control columns. Each of the remaining two columns received the effluent of the MP reactor or the effluent of the LP reactor. The GAC in the later two columns and one of the control columns was reactivated GAC acquired directly from the reactivation facility at Richard Miller Treatment Plant (RMTP). The second control column included GAC produced by an alternative regeneration process. The GAC was bituminous coal, US mesh size 12x40 with 0.55-0.75 mm effective size, and apparent density of 0.48 g/cm³ (30 lbs/ft³) The GAC bed depth in the 10.2 cm (4 inch) diameter columns was about 173 cm (68 inches), and the empty bed contact time (EBCT) was set to 15 minutes to simulate RMTP full-scale GAC contactor operation. The GAC column skids also included clearwells and a backwash system.

The last pieces of equipment in the pilot process line were four annular reactors (Biosurface Technologies, model 1120 LS), which were connected to the effluent lines of the GAC columns. (See Figure A.3.) The annular reactors were chosen to simulate a velocity of a typical water distribution main and are described further in the analytical methodologies section.
Figure A.1: Pilot plant schematic at GCWW
Figure A.2: UV pilot equipment at GCWW (a) MP Reactor, (b) LP reactor, (c) GAC pilot contactors

Figure A.3: Annular reactor for biofilm tests
A.2 Pilot Plant Operation

The pilot study was structured in a way that would address the multiple research objectives within a period of 12 months. In order to capture the seasonal variations of the influent water quality, the selected contaminants were spiked quarterly, and the same parameters were consistently monitored. The pilot unit was constructed in the summer of 2007 and the tests began in the fall of 2007. Figure A.4 shows the process schematic of the pilot unit with the sampling points.

The pilot unit was operated continuously for twelve consecutive months. During each quarter there were three phases of testing: (a) UV advanced oxidation with CONV influent water, (b) UV advanced oxidation with Post-GAC influent water, and (c) UV photolysis with Post-GAC influent water. For both UV advanced oxidation phases the operation of the system was based on performance. The goal was to operate the advanced oxidation system so that atrazine would degrade by 80% through both the MP and LP reactor trains. The hydrogen peroxide concentration was maintained at 10 mg/L at all times (except during the UV photolysis testing) and the UV dose was adjusted by changing the flow through the reactors, and for the MP reactor by adjusting the power levels. Since the UV\textsubscript{T254} and TOC concentration of the water varied seasonally, tests were performed at the beginning of each phase using atrazine to determine the operational conditions of the UV reactors. An 80% atrazine degradation (or analogous MTBE degradation) was targeted for the UV/H\textsubscript{2}O\textsubscript{2} phases to determine the operational conditions of the UV reactors. MTBE was also used during those tests until the relationship between the degradation of atrazine and MTBE was established, and then MTBE was used as a surrogate since its analysis was much easier and faster than
atarazine’s. Once the flow and power level were determined for both reactors, the solution of contaminants was spiked into the pilot influent to determine the degradation of all the contaminants at those conditions. The above method was followed with both CONV and Post-GAC pilot influent. Following the Post GAC advanced oxidation phase, the hydrogen peroxide feed was discontinued, the UV dose at the reactors was set at the lowest level and the contaminant spiking was repeated. When the three phases were completed, the pilot influent was switched to CONV water and the reactors and flows were set at the 80% atrazine degradation conditions until the next quarter began.

Every time that the water in the pilot was switched, the cast iron pump for either the CONV or Post-GAC water was primed to avoid potential fouling of the sleeves. The sleeve in the MP reactor was wiped on a daily basis with the manual rubber wiper. At the beginning of each quarter the pilot was shut down to have the sleeves of both reactors cleaned. The reactors were drained and the sleeves were removed and cleaned with 0.1N HCl solution and finally rinsed. Before the sleeves were placed back, the inside of the reactors was wiped and the UV sensors were removed and wiped with isopropyl alcohol. The GAC columns were backwashed on a regular basis, about once per week, except during the spring season where they required more frequent backwashing due to air-binding.

During the 12 month study several water quality, operational and performance parameters were monitored at the pilot, as shown in Table A.1. The pilot was monitored on a daily basis for flows, UV reactor intensity and applied UV dose. The UV T$_{254}$ of the pilot influent was monitored and the hydrogen peroxide concentration was determined before and after the reactors and after the GAC contactors. Additionally several other
water quality parameters, such as TOC, alkalinity, nitrate and nitrite were tested at various frequencies across the pilot. The analytical methods for these tests are also shown in Table A.1.

Figure A.4: Pilot plant process schematic at GCWW
Table A.1: Water quality sampling protocol and pilot performance monitoring

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1. AWWA Standard Methods for Examination of Water and Wastewater.

2. The methods for hydrogen peroxide measurement are described in the Materials and Analytical Methodologies section.
A.3 Additional Procedures

The hydrogen peroxide used at the pilot unit was 35% Oxypure Grade from FMC. It was diluted to 8% with RO water in day tanks, and its exact concentration was measured by permanganate titration. According to this method about 10 mL of the 8% hydrogen peroxide was weighted and then washed into a 250 mL volumetric flask with RO water and mixed thoroughly. Twenty-five milliliters were transferred in a 400 mL beaker containing 250 mL RO water and 10 mL sulfuric acid, and it was titrated to a permanent pink color with 0.3N potassium permanganate.

Hydrogen peroxide was dosed at 10 mg/L at the pilot influent and samples from all pilot locations were measured daily. The method used initially was iodometric titration with a hydrogen peroxide test kit (model HYP-1) by Hach, and it was replaced during the second quarter of testing with a spectrophotometric analysis provided by KWR method LAM-048. According to this method either 5 or 10 mL of the water sample (depending on expected H₂O₂ concentration) was transferred to 100 mL flask, followed by 8 mL of 1.8 M sulfuric acid and 2 mL of Potassium bis(oxalate)oxotitanate(IV) dehydrate (K₂[TiO(C₂O₄)₂]·2H₂O), and then the flask was filled with RO water and mixed. After 15 minutes the sample was transferred to a 5 cm cell and analyzed using a spectrophotometer at 400 nm. The measurement was converted to H₂O₂ concentration based on a calibration curve.
A.4 Results and Discussion

A.4.1 Background Water /Operational

The pilot unit was in continuous operation from October of 2007 until October 2008. During that period the pilot influent water showed seasonal variations or changes in water quality due to natural surface water fluctuations and the upstream treatment processes. The influent water quality parameters potentially affecting the performance of the UV advanced oxidation process were UVT$_{254}$, TOC concentration, alkalinity and iron concentration. Influent UVT$_{254}$ and TOC concentration were expected to fluctuate during the year especially for the CONV pilot influent water, which was used most of the time during the pilot study.

The changes in UVT$_{254}$ for the CONV and the Post GAC water can be seen in Figure A.5. The CONV water UVT$_{254}$ ranged between 84 and 95%/cm, with its lowest points being in December 2007 and the summer of 2008. The UVT$_{254}$ of the Post-GAC water was more stable and fluctuated only between 95-98%/cm. The variation in UVT$_{254}$ greatly affected the operation of the UV reactors and changes in flow and power level were required in order to achieve the required 80% atrazine degradation.
The TOC concentration of the pilot influent water also changed during the 12 month study, fluctuating between 1.2-2.6 mg/L for the CONV water and 0.6-1.0 mg/L for the Post-GAC water. Figure A.6 and Figure A.7 show the influent TOC concentration of the pilot versus the TOC values at the effluent of each reactor. On average a slight 2-3% decrease in TOC concentration was observed through both reactors when CONV was the pilot influent water, while when Post-GAC influent water was used the decrease in TOC concentration through the reactors was on average 4-7%. This consistent small decrease of TOC through the UV reactors can be explained by the mineralization of natural organic matter (NOM) by the hydroxyl radicals formed in the reactors. Due to their redox potential of 2.8V, hydroxyl radicals have the potential of completely oxidizing organic molecules to carbon dioxide (Carr and Baird, 2000). Research has shown that
under advanced oxidation conditions similar to the ones applied in this study, NOM was not mineralized but partially oxidized resulting in a shift of the NOM’s molecular weight distribution towards smaller organic molecules. However, when prior treatment processes remove higher molecular weight fractions of NOM as indicated by the drop in SUVA values, then UV/H₂O₂ at similar conditions used in this study may cause mineralization of NOM (Sarathy and Mohseni, 2007 and 2009). The CONV pilot influent water had already been processed by coagulation, flocculation and filtration which removed part of the TOC found in the river water, while the Post GAC had an additional removal of TOC due to adsorption. The reduction in SUVA values between the river, CONV, and Post-GAC water is very likely the reason that mineralization of TOC was observed through the UV reactors during the UV/H₂O₂ process.

Figure A.6: TOC through the MP Reactor. (■) TOC Influent, (□) TOC Effluent
Alkalinity also exhibited seasonal variations as shown in Figure A.8, and it varied between 49-82 mg/L for both CONV and Post-GAC water. Since alkalinity is also a scavenger of hydroxyl radicals, it was monitored for the influent and effluent of the UV reactors, but no significant or consistent changes were observed through the UV/H₂O₂ process. Iron was below the detection limit (20 µg/L) for the duration of the study.
The pilot influent water contained low concentrations of nitrate, which varied seasonally between 0.5-1.3 mg/L (as nitrogen), and nitrite was below the limit of detection, as shown in Figure A.9. About 10-20% of the nitrate was converted to nitrite through the MP reactor, under the operating conditions of the system, as the lamp sleeves were not doped to eliminate this transformation. However, the nitrite concentrations were much lower than the U.S. regulated Maximum Contaminant Level (MCL) of 1 mg/L. Depending on influent nitrate concentration and the local regulations, unchlorinated systems may wish to use doped sleeves to reduce nitrate reduction. The sum of the nitrate and nitrite effluent concentrations exiting the MP reactor matched the reactor influent concentration of nitrate relatively well. This total nitrate-nitrite concentration also was below the U.S. regulated MCL of 10 mg/L as N. As expected
there were no changes in the nitrate through the LP reactor and no formation of nitrite was observed as depicted in Figure A.10.

**Figure A.9:** Nitrate-Nitrite-Medium Pressure Reactor. (■) Nitrate Influent, (□) Nitrate Effluent, (♦) Nitrite Influent, (◊) Nitrite Effluent, (▲) Nitrate+Nitrite Effluent

**Figure A.10:** Nitrate-Nitrite-Low Pressure Reactor. (■) Nitrate Influent, (□) Nitrate Effluent, (♦) Nitrite Influent, (◊) Nitrite Effluent
The influent and effluent hydrogen peroxide concentration of the UV reactors and GAC contactors was measured on a daily basis. The pilot influent peroxide averaged 10 mg/L (St.D. 0.5 mg/L), while the MP effluent had an average of 8.9 mg/L (STD = 0.5 mg/L), and the LP effluent 9.2 mg/L (STD = 0.6 mg/L). Therefore, the hydrogen peroxide consumption was higher through the MP reactor than the LP reactor in order to achieve the same percentage of atrazine degradation. Hydrogen peroxide was never detected at the effluent of the GAC contactors, indicating that it was completely adsorbed/decomposed through the existing GAC beds. A side effect of the peroxide decomposition was the slow formation of gas in the GAC beds receiving the effluent of the UV reactors, which was more intense and visible during the spring months when the temperature of the influent water was rising, and the ambient temperature in the facility was higher.

The initial method used to analyze hydrogen peroxide through the pilot was an iodometric method, which gave accurate results for all sample points except for the effluent of the MP reactor and the effluent of the consecutive GAC contactor. The results of the MP effluent were 2-3 mg/L higher than the influent hydrogen peroxide, and the effluent of the GAC contactor showed a similar 3 mg/L breakthrough of hydrogen peroxide when this method was used. The analysts were not able to determine the cause of these anomalies, thus an alternative spectrophotometric method was developed (KWR, LAM-048). The spectrophotometric method was not subject to these errors and no new interferences were found.
A.4.2 Contaminant Degradation

A.4.2.1 UV/H$_2$O$_2$ with CONV pilot influent water

A primary operational goal of the pilot study was to consistently set the UV reactors at the proper UV dose that would achieve the benchmark 80% atrazine degradation. This became particularly challenging when CONV influent water was used, since the UVT$_{254}$ of the water fluctuated significantly throughout the year, and different UV doses were required to keep the atrazine degradation constant. To achieve these conditions throughout the study, UV doses between 200-500 mJ/cm$^2$ were required for the MP reactor and doses between 1200-2000 mJ/cm$^2$ were required for the LP reactor (based on the manufacturer’s UV dose tables). As shown in Figure A.11, atrazine reduction was between 75-85% for most of the study quarters, with the only exception being the first quarter of the study when it was measured at 62% for the LP reactor. The reason for the low value the first quarter was likely iron fouling of the LP reactor sleeves because of an improperly primed pump. After the sleeves were cleaned the LP reactor could provide sufficient UV dose to reach the benchmark.

Figure A.11: Contaminant degradation by UV/H$_2$O$_2$ in CONV water (a) MP Reactor, (b) LP reactor. (■) Fall 2007, (■) Winter 2008, (■) Spring 2008, (■) Summer 2008
With the exception of MTBE, the remaining six contaminants showed higher reduction rates than atrazine for most quarters. Their average destruction in the CONV water is presented in A.2., with 17 α-Ethynylestradiol (EE2) having the highest percent destruction at 98% and MTBE the lowest at 54%. The overall order of degradation was: MTBE<Atrazine<Ibuprofen<MIB<Metolachlor=Gemfibrozil< 17-α-Ethynylestradiol

There were no significant differences in contaminant destruction between the MP and the LP reactors at the 80% atrazine level, which could be an indication that the primary mechanism of destruction is the reaction with hydroxyl radicals, with photolysis probably playing a less significant role. Rosenfeldt and Linden (2004) drew a similar conclusion when comparing the destruction of EDCs by photolysis and advanced oxidation with MP and LP lamps. Additionally, the aforementioned order of degradation is similar to the order of the reaction rate constants with hydroxyl radicals (k_{OH}) for these contaminants, with MTBE having the lowest reported value at 1.6 \cdot 10^9 and 17-α-Ethynylestradiol having the highest reported value of 1.08 \cdot 10^{10}. Therefore, it would be expected for MTBE to present the lowest destruction among the other contaminants.

Table A.2: Average degradation of contaminants (%) by the UV reactors with CONV influent water

<table>
<thead>
<tr>
<th>contaminant</th>
<th>Atrazine</th>
<th>MTBE</th>
<th>Metolachlor</th>
<th>MIB</th>
<th>EE2</th>
<th>Gemfibrozil</th>
<th>Ibuprofen</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP</td>
<td>84</td>
<td>54</td>
<td>96</td>
<td>90</td>
<td>98</td>
<td>92</td>
<td>87</td>
</tr>
<tr>
<td>LP</td>
<td>74</td>
<td>56</td>
<td>87</td>
<td>85</td>
<td>93</td>
<td>92</td>
<td>82</td>
</tr>
</tbody>
</table>
A.4.2.2 UV/H₂O₂ with Post-GAC pilot influent water

When the higher UVT₂₅₄ Post-GAC water was used as influent to the pilot reactors, adjustments to their flow and power level were made to reach the 80% atrazine degradation conditions. As shown in Figure A.12, these conditions were met closely for both reactor types for almost all study quarters. Again, all the other contaminants except MTBE exhibited higher overall percent destruction than atrazine, and as shown in Table A.3, the average destruction results are similar for both MP and LP reactors.

By comparing the average values in Table A.2 and Table A.3, it can be seen that most of the contaminants the average degradation levels were very similar for the CONV and Post-GAC water. Therefore, the difference in UVT₂₅₄ and TOC content of the influent water did not affect the degree of contaminant degradation when the reactors were benchmarked based on performance.
**Figure A.12**: Contaminant degradation by UV/H$_2$O$_2$ in Post-GAC water (a) MP Reactor, (b) LP reactor. (■) Fall 2007, (■) Winter 2008, (■) Spring 2008, (■) Summer 2008

**Table A.3**: Average degradation of contaminants (%) by the UV reactors with Post-GAC influent water

<table>
<thead>
<tr>
<th></th>
<th>Atrazine</th>
<th>MTBE</th>
<th>Metolachlor</th>
<th>MIB</th>
<th>EE2</th>
<th>Gemfibrozil</th>
<th>Ibuprofen</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP</td>
<td>84</td>
<td>51</td>
<td>95</td>
<td>88</td>
<td>94</td>
<td>93</td>
<td>85</td>
</tr>
<tr>
<td>LP</td>
<td>81</td>
<td>58</td>
<td>95</td>
<td>91</td>
<td>96</td>
<td>95</td>
<td>84</td>
</tr>
</tbody>
</table>

**A.4.2.3 UV photolysis with Post-GAC pilot influent water**

In addition to the UV/H$_2$O$_2$ experiments, tests were performed to examine the degradation of contaminants by photolysis using Post-GAC as pilot influent. Since the two reactor types could provide significantly different UV dose ranges, the photolysis tests were performed at the low end of UV doses for each reactor, which were around 280 mJ/cm$^2$ for the MP reactor and 800 mJ/cm$^2$ for the LP reactor (as estimated by the supplier’s UV dose tables). Figure A.13 shows the results for the MP and LP reactors, where the contaminant degradation by the MP reactor was significantly higher than that of the LP reactor even if the UV dose was almost a third of the MP dose. That
demonstrates the advantage of the MP reactor during a photolysis process due to the effect of the wide UV spectrum on the destruction of various types of bonds.

Additionally, atrazine, metolachlor, and 17 α-ethynylestradiol underwent significant degradation by photolysis through the MP reactor, not appreciably less than their UV/H₂O₂ destruction levels. These excellent results are in part due to the very high UVT₂₅₄ of the Post-GAC pilot influent water. The remaining contaminants exhibited less than 50% removal by photolysis through the MP reactor compared to UV/H₂O₂.

However, part of the degradation may be attributed to the formation of hydroxyl radicals by the UV photolysis of the background dissolved organic carbon (Pereira et al., 2007).

**Figure A.13:** Contaminant degradation by UV photolysis in Post-GAC water (a) MP Reactor, (b) LP reactor. (■) Fall 2007, (●) Winter 2008, (■) Spring 2008, (●) Summer 2008

**A.4.2.4 E_EO for UV photolysis with Post-GAC pilot influent water**

All of the contaminants showed degradation under UV/H₂O₂ and photolysis conditions for both MP and LP reactors. However, the energy required for a log removal of each contaminant under the two processes varies significantly with the reactor type and contaminant. Figure A.14 and Figure A.15 show the estimated E_EO values for UV/H₂O₂ and UV photolysis for the MP and LP reactor respectively, and they have been plotted...
in the same scale to illustrate their differences. For all of the tested contaminants UV/H\textsubscript{2}O\textsubscript{2} required the least amount of energy for a log removal compared to photolysis (See Table A.4 and Table A.5.) regardless of the type of UV lamp. 17-\(\alpha\)-ethynylestradiol had the lowest \(E_{\text{EO}}\) for photolysis, which is only 1.5-2 times higher than its UV/H\textsubscript{2}O\textsubscript{2} \(E_{\text{EO}}\) with either the MP or LP reactor, while MTBE had the highest photolysis \(E_{\text{EO}}\) being 4-5 times higher than the equivalent \(E_{\text{EO}}\) with UV/H\textsubscript{2}O\textsubscript{2}. This indicates that 17-\(\alpha\)-ethynylestradiol is much more susceptible to photolysis than MTBE, and it may be economically feasible to use only photolysis for its removal, while for MTBE UV/H\textsubscript{2}O\textsubscript{2} may be the best treatment choice since it requires far less energy compared to photolysis. Finally, for most of the contaminants, the \(E_{\text{EO}}\) ratio between UV photolysis and UV/H\textsubscript{2}O\textsubscript{2} is lower for the MP reactor than the LP reactor, indicating that photolysis was more effective for the MP than the LP reactor, potentially due to the wider UV spectrum, which could photolyse different types of bonds. Specifically, atrazine has a high UV absorption rate at wavelengths less than 250 nm and also has a high photolysis quantum yield at this range, consequently UV photolysis by MP lamps is more efficient than photolysis by LP lamps (Sharpless and Linden, 2005). Similarly, MIB has very low UV molar absorption at 254 nm, and much higher absorption at lower wavelengths, thus presenting greater degradation by photolysis and lower \(E_{\text{EO}}\) with the MP lamps versus the LP lamps (Rosenfeldt et al., 2005).
Figure A.14: Contaminants $E_{EO}$ for MP reactor in Post-GAC water by (a) UV/H$_2$O$_2$, (b) UV photolysis. (■) Fall 2007, (■) Winter 2008, (■) Spring 2008, (■) Summer 2008 (1 kWh/m$^3$-order = 3.7854 kWh/kgal-order)

Table A.4: Average $E_{EO}$ (kWh/m$^3$-order) of contaminants for MP reactor under UV/H$_2$O$_2$ and UV photolysis (1 kWh/m$^3$-order = 3.7854 kWh/kgal-order)

<table>
<thead>
<tr>
<th></th>
<th>Atrazine</th>
<th>MTBE</th>
<th>Metolachlor</th>
<th>MIB</th>
<th>EE2</th>
<th>Gemfibrozil</th>
<th>Ibuprofen</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV/H$_2$O$_2$</td>
<td>0.41</td>
<td>0.90</td>
<td>0.23</td>
<td>0.32</td>
<td>0.25</td>
<td>0.27</td>
<td>0.43</td>
</tr>
<tr>
<td>UV photolysis</td>
<td>0.72</td>
<td>4.42</td>
<td>0.42</td>
<td>1.40</td>
<td>0.36</td>
<td>1.09</td>
<td>1.02</td>
</tr>
<tr>
<td>$E_{EO}$ Ratio UV photolysis / UV/H$_2$O$_2$</td>
<td>1.8</td>
<td>4.9</td>
<td>1.8</td>
<td>4.4</td>
<td>1.4</td>
<td>4.0</td>
<td>2.4</td>
</tr>
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</table>
Figure A.15: Contaminants $E_{EO}$ for LP reactor in Post-GAC water by (a) UV/H$_2$O$_2$, (b) UV photolysis. (■) Fall 2007, (▲) Winter 2008, (■) Spring 2008, (▲) Summer 2008 (1 kWh/m$^3$-order = 3.7854 kWh/kgal-order)

Table A.5: Average $E_{EO}$ (kWh/m$^3$-order) of contaminants for LP reactor under UV/H$_2$O$_2$ and UV photolysis (1 kWh/m$^3$-order = 3.7854 kWh/kgal-order)

<table>
<thead>
<tr>
<th></th>
<th>Atrazine</th>
<th>MTBE</th>
<th>Metolachlor</th>
<th>MIB</th>
<th>EE2</th>
<th>Gemfibrozil</th>
<th>Ibuprofen</th>
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</thead>
<tbody>
<tr>
<td>UV/H$_2$O$_2$</td>
<td>0.18</td>
<td>0.31</td>
<td>0.10</td>
<td>0.12</td>
<td>0.10</td>
<td>0.10</td>
<td>0.17</td>
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<tr>
<td>UV photolysis</td>
<td>0.56</td>
<td>1.31</td>
<td>0.30</td>
<td>0.82</td>
<td>0.19</td>
<td>0.63</td>
<td>0.68</td>
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<tr>
<td>$E_{EO}$ Ratio UV photolysis / UV/H$_2$O$_2$</td>
<td>3.1</td>
<td>4.2</td>
<td>2.9</td>
<td>6.7</td>
<td>1.9</td>
<td>6.2</td>
<td>3.9</td>
</tr>
</tbody>
</table>

A.5 References


Pereira, V.J.; Weinberg, H.; Linden, K. G. and Singer, P. C. (2007) UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and


Appendix B

Collimated Beam Background and Procedures
Collimated Beam Background and Procedures

B.1 Introduction

MTBE was introduced in the late 1970’s as a gasoline additive replacing tetra-ethyl lead. Oxygenates, such as MTBE, increase oxygen levels in gasoline to promote a more complete burning of gasoline which reduce air emissions of carbon monoxide, ozone and other volatile organic compounds. MTBE is a volatile and flammable, organic compound that is highly soluble (See Table B.1.). Due to its unique chemical properties, resistance to biodegradation and hydrophilic nature, MTBE poses a threat environmentally. These properties, along with its widespread use, have led to MTBE contamination of ground and surface waters. Currently, national regulations do not exist; however, in 1997, the USEPA issued a drinking water advisory stating that concentrations of 20-40 µg/L or below will not pose a threat. The USEPA has recognized MTBE as a potential carcinogen at high exposure levels and has been placed on the Contaminant Candidate List (CCL 3).
The effectiveness of potential drinking water treatment techniques for MTBE is determined by the physical and chemical properties of this compound. Granular activated carbon (GAC) can be used for destruction of MTBE, but due to the high solubility of MTBE, GAC reactivation must be frequent. Air stripping, a treatment technology based on Henry’s constant, has also been considered. MTBE has a lower Henry’s constant than other organic compounds treated by air stripping; therefore this treatment has been shown to be difficult and costly. Advanced oxidation processes are promising technologies for the destruction of MTBE. Specifically, the UV/H$_2$O$_2$ process has received the most attention, and the kinetics and reaction mechanisms have been well-studied (Cooper, 2009).

The UV/H$_2$O$_2$ process destroys contaminants directly in the water through oxidation. The first step is the generation of hydroxyl radicals. The O-O bond in hydrogen peroxide is cleaved by ultraviolet (UV) light creating highly oxidized hydroxyl radicals (Zang, 2003). The hydroxyl radicals attack the MTBE molecule through H-abstraction, which can occur from either the methoxy group or any methyl group. The methoxy group of the MTBE molecule is most prone to H-abstraction due to the electrophilicity of hydroxyl radicals and the stereoelectronic effect of the group (Stefan, 2000). The hydroxyl radical

### Table B.1: Chemical and Physical Properties of MTBE

<table>
<thead>
<tr>
<th>Physical and Chemical Properties</th>
<th>MTBE</th>
<th>Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight (g/mole)</td>
<td>88</td>
<td>78</td>
</tr>
<tr>
<td>Water Solubility (mg/L) @ 25°C</td>
<td>43,000-54,300</td>
<td>1730</td>
</tr>
<tr>
<td>Henry’s Constant at 25°C</td>
<td>0.018</td>
<td>0.23</td>
</tr>
<tr>
<td>Organic Carbon Partitioning Coefficient (Log $K_{OC}$)</td>
<td>1.091-1.049</td>
<td>1.18-2.16</td>
</tr>
</tbody>
</table>
is non-selective; therefore any organic or inorganic compound in the water can scavenge radicals leading to ineffectiveness of this technology.

**B.2 Materials and Methods**

The study was conducted using a low-pressure, bench scale collimated beam unit. The unit is designed to irradiate batch liquid samples in a controlled manner. The top of the unit houses four low-pressure, mercury, ultraviolet (germicidal) lamps (15W). UV light exposure is controlled by a shutter and an open petri dish sits upon a stir plate that is 30 cm away from the lamps. The UV dose (or fluence) is controlled by the amount of time the batch sample is left in the unit. Irradiation time and UV dose were calculated by accounting for a variety of factors including radiometer readings, surface reflection, sample depth, UV transmittance, and petri factor based on work by Bolton and Linden (2003). (See Figure B.1.)
Precision studies were initially performed to ensure MTBE concentration (4 µg/L) and hydrogen peroxide concentration (10 mg/L). After determining irradiation times for desired UV doses, a 100 mL batch sample of MTBE-spiked source water was placed in the collimated beam unit with the shutter in place. Ten mg/L hydrogen peroxide was added to the petri dish and after mixing for 10 seconds, the shutter was pulled and the sample was irradiated for the pre-determined amount of time. Samples were analyzed following USEPA 524.2. A simulated blank sample was irradiated at the highest UV
dose at the end of every experiment. This sample contained the initial target MTBE concentration and was performed with the shutter in place, so that the sample was not irradiated. This simulation ensured that there was no volatilization of MTBE. Photolysis experiments (no H₂O₂) were also conducted so that comparisons could be made to UV/H₂O₂ treated samples.

B.3 Results

Figure B.2 depicts the difference in MTBE destruction for several UV fluences (doses) in laboratory pure water. The lower curve UV with photolysis alone shows considerably less destruction than the upper curve with 10 mg/L H₂O₂.

Figure B.2: Photolysis (no H₂O₂) vs. UV/H₂O₂ 10 mg/L H₂O₂- Post-GAC
Figure B.3 depicts MTBE destruction with $\text{H}_2\text{O}_2$ concentration ranging from 0 to 30 mg/L in laboratory pure water and CONV water at 600 mJ/cm$^2$. At a $\text{H}_2\text{O}_2$ concentration of 8 mg/L the destruction of MTBE reaches a plateau. However, no plateau is reached for the CONV water. Although the trends are similar at 1000 mL/cm$^2$, the destruction reaches almost 100 percent for the CONV water with 30 mg/L $\text{H}_2\text{O}_2$. (See Figure B.4.)

**Figure B.3:** UV/$\text{H}_2\text{O}_2$ varying $\text{H}_2\text{O}_2$ DI & CONV 600 mJ/cm$^2$
Figure B.4: UV/H$_2$O$_2$ varying H$_2$O$_2$ DI & CONV 1000 mJ/cm$^2$

Figure B.5 depicts the destruction of MTBE over an MTBE concentration range of 2 to 70 µg/L at 600 mJ/cm$^2$ in laboratory pure water. The destruction of MTBE is very similar over this range, trending downward very slightly (approximately 2%) in a linear fashion.
Figure B.5: UV/H₂O₂-Varying initial MTBE conc. over environmentally relevant concentration range DI water - 600 mJ/cm²

B.4 References


Procedure for Collimated Beam

**Chemicals:**

<table>
<thead>
<tr>
<th>Chemicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTBE(1000ppm)</td>
</tr>
<tr>
<td>Hydrogen peroxide ($H_2O_2$)</td>
</tr>
<tr>
<td>Sodium sulfite ($Na_2O_3S$)</td>
</tr>
<tr>
<td>Sulfuric acid ($H_2SO_4$) 1.8 M</td>
</tr>
<tr>
<td>Potassium bis(oxalate)oxotitanate(IV) dihydrate solution ($K_2[TiO(C_2O_4)_2] \cdot 2H_2O$)</td>
</tr>
</tbody>
</table>

**Materials:**

<table>
<thead>
<tr>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volumetric Flasks: 1L (2), 2L (1), 50mL(1), 100mL (# of samples)</td>
</tr>
<tr>
<td>Class A Pipets: 10mL (1), 8mL(1), 100mL (1), 1mL(1), 5mL (# of samples)</td>
</tr>
<tr>
<td>Micropipettor and tip</td>
</tr>
<tr>
<td>40 mL amber vials</td>
</tr>
<tr>
<td>Peroxide Method Supplies</td>
</tr>
<tr>
<td>Radiometer</td>
</tr>
</tbody>
</table>

1) Turn the LP-UV light of the collimated beam (cb) box on and allow to warm up.

2) Obtain variables needed for dose calculations (ex: time of each dose):

   a. $\text{UV}_{254}$ absorbance reading of source water using the 1cm cell
      
      - Choose the “single wavelength” option
      - Zero the spectrometer with RO water and then take reading of source water (measure in absorbance)
b. Obtain central radiometer reading (lamp in collimated beam box must be on for at least 10 minutes):

- Measure the distance from the lamp to the top of the first line on the radiometer end, it should be 30 cm apart.

- After the UV lamp has been on for about 10 minutes, uncap end of radiometer and place on jack. The measuring end of the radiometer should be placed in the center of the jack which is measured by the cross on the top of jack.

- Remove shutter, close door and once radiometer comes to a somewhat steady value, take reading.

c. Add the two readings to the Excel spreadsheet to obtain time of doses.

- For spreadsheet, go to the J: / Drive followed by UV/H₂O₂, then Collimated Beam, and Trials and then open file that reads “Fluence Time Calculation”

- Enter obtained values in appropriate fields on spreadsheet, adjust UV dose as necessary and acquire UV dose time.

3) Place 2 scoops of sodium sulfite in 40 mL amber vials and label (except for samples that do not have H₂O₂)
4) Make up serial dilution to get a 4 ppb MTBE stock solution in chosen source water (ex of source water: DI, GAC Influent, and GAC Effluent). Stock solution can be placed in a 2 L amber bottle.

   a. 10 mL of 1000ppm into 1L = 10 ppm MTBE
   b. 8 mL of 10 ppm into 1 L = 80 ppb MTBE
   c. 100 mL of 80 ppb into 2 L = 4 ppb MTBE

5) Make up 0.7 % H₂O₂ solution in RO Water

   a. 1 mL of 35 % H₂O₂ into 50 mL = 0.7 % H₂O₂
   b. Run UV 254 reading to check concentration

6) Fill 3- 40mL amber vials head space free with 4 ppb MTBE stock solution; these are the blank samples of stock solution (total of 3 blanks)

7) Pipet 100 mL of stock solution in Petri dish (pipet from stock solution right before each sample is placed in the box)

8) Micropipette 136 µL (or desired dose) of the 0.7% H₂O₂ solution into the Petri dish

9) Place the Petri dish on the jack inside the collimated beam- start stir bar and adjust so that there is no vortex. Let sample mix for at least 10 seconds then pull shutter and start timer

10) If varying peroxide dosing, then pipet 5 mL of Petri dish solution into 100 mL volumetric flask before and after UV irradiation, for later spectrophotometric analysis and adjust values in Excel spreadsheet (ex: volume)
11) Run sample for time allotted as calculated from excel spreadsheet

12) After time elapses, replace shutter and remove sample

13) Fill 2-40 mL amber vials with sample headspace free. (sample + duplicate)

14) At the highest UV dose, run a simulated blank without pulling the shutter.

*** If varying peroxide dosing, run spectrophotometric analysis of peroxide for all samples (the before and after 5mL quantity taken from sample). See below for procedure.
Appendix C

Biofilm Potential Methodologies
Biofilm Potential Methodologies

C.1 Biofilm Methodologies

The annular reactor methodology for biofilm formation was developed by Sharp, et al. (2001) to assess the adherence and growth of bacterial populations on pipe surfaces in the distribution system. To make this assessment, it is important to simulate pipe materials, pipe velocities and make use of indigenous organisms and natural nutrient levels, i.e. ratio of organic carbon to nitrogen to phosphorous. Pipe velocities greatly affect the ability of microbes to attach to pipe interiors. High pipe velocities can cause shearing of the biofilm. Donlan and Pipes (1988) concluded that water velocity had an inverse relationship with biofilm counts. Servais (1989) elucidated the importance of using indigenous microorganisms to give a realistic of actual plant conditions. The annular reactor is able to measure the biofilm regrowth potential of continuous plant and distribution streams utilizing actual distribution conditions. It contains coupons as surfaces for biofilm growth. These coupons can be made of various pipe materials, and the unit can be set to simulate a range of pipe velocities.

Annular reactors were used to assess biofilm potential after GAC adsorption in unchlorinated process streams. Four model 1320LS Laboratory Annular Reactors from BioSurface Technologies Corp. received flow from the effluent of the four GAC columns. The experiment ran from September 4, 2008 to October 2, 2008, which corresponded to run-day 300 to 328 of the GAC. Before being placed in service, the reactors were disassembled and thoroughly cleaned, and then the polycarbonate coupons were inserted into the designated slots in the carousels. The components were moistened with deionized water and autoclaved for 15 minutes. The sterilized units were
reassembled on site with motors and controllers and set to a flow rate of 8 mL/minute and a carousel rotational speed of 90 revolutions per minute. These conditions simulated a pipe velocity of 0.30 meters per second (1 foot/second). The rotational speed and flows were monitored bi-weekly.

The biofilm was quantified by heterotrophic plate count and ATP bioluminescence analysis. At the end of the annular reactor run, the coupons were removed using sterile technique and appropriate quality control. The biofilm from six coupons per reactor were analyzed by heterotrophic plate count (HPC) analysis. A sterile, disposable cell scraper with a flexible blade was used to remove biofilm from the polycarbonate coupons. The blade was as wide as the coupon, so a single pass with either side of the blade was made. The blade portion of the scraper was removed and added to a sterile centrifuge tube. The coupon was then rinsed with 1 mL of sterile phosphate buffered water, collected in the centrifuge tube with the scraper. The centrifuge tubes were all initially vortex mixed for 60 seconds and sonicated for 5 minutes to break up and homogenize the biofilm. Another 30 second mixing was performed just prior to removing a 0.1 ml aliquot of the solution. This aliquot was used to make dilutions of 0.01, 0.001, and 0.0001 ml for heterotrophic plate count analysis. All dilutions were plated out using a 0.1 ml sample dilution volume and the pour plate technique, to find one countable plate per coupon (Standard Methods 9215 B).

The biofilm was removed from 12 coupons per reactor for the bioluminescence procedure. A sterilized hemostat was used to raise and secure the coupon, leaving only the bottom 1 centimeter of the coupon still within the tube for support. The cap of the Utrasnap bioluminescence pen was removed and the swab withdrawn using sterile
technique. The exposed surface of the coupon was wiped in thirds from left to right, top to bottom using three firm and consistent strokes. The swab was rotated to an unused section after each stroke. The swab was then returned to the bioluminescence tube and recapped. This process was repeated for each coupon.

The bioluminescence methodology is based on detection of adenosine -5'-triphosphate (ATP) in metabolically active cells. ATP is involved in all aspects of metabolism, and, therefore, can be used to determine the viability of microbial cells. ATP disappears within two hrs of living matter death (Driebel 2008).

The firefly luciferase-based (bioluminescence) assay for detecting ATP was established by Bautista et al. (1994) as a way to rapidly monitor microorganisms on surfaces. Satoh et al. (2004) developed an additional method to increase the sensitivity of the bioluminescence assay. They developed the polyphosphate-ATP amplification reaction. This amplification reaction employs adenylate kinase, to converts adenosine monophosphate and ATP to two molecules of adenosine diphosphate (ADP); and polyphosphate (polyP) kinase, which converts two molecules of ADP back to two molecules of ATP. Using these reactions, ATP is amplified exponentially, resulting in high levels of bioluminescence in the firefly luciferase reaction (Asami et al., 2006).

If ATP in microorganisms or cells is to be measured, it must be extracted efficiently without allowing it to degrade. A wide variety of ATP-extracting reagents have been described (Karl, 1980, Stanley, 1986). Generally, the best solvent for extraction is trichloroacetic acid (TCA). TCA efficiently releases ATP from microorganisms and cells while inactivating enzymes that might quickly degrade the ATP before measurement.
Because excessive TCA inhibits the bioluminescence reaction, the lowest concentration of TCA needed for extraction is used. (Karl, 1980; Stanley, 1986)

A luminometer was used to quantify the ATP bioluminescence. It gives a direct measurement of the light intensity and therefore a direct quantification of ATP. The light is quantified as relative light units (RLU), and the intensity of the emission is proportional to the concentration of ATP. Bioluminescence was measured using a Hygiena System SURE Plus luminometer. Luminometer performance was monitored by analysis of two standard rods with known assigned values. Analysis of these standard rods occurred at the beginning and end of the luminometer analysis. Three readings were taken of each standard. The readings had to be within 20% of each other, and the average value had to be within 20% of the assigned value of the rods, for acceptable QC. Coupon samples were processed by removing the swab from the pen, carefully wiping the entire upper surface of each coupon as described above, then returning the swab into the pen. The pen was later activated by breaking the internal snap valve in the top bulb, and bending the pen bulb back and forth, squeezing twice. The swab tip was bathed in the expelled reagent by gently shaking the test pen for five seconds. The test pen was wiped with a laboratory tissue and inserted into the luminometer and the top was closed. Triplicate readings were taken after a 15 second stabilization period, and an average reading calculated. The process was repeated with each sample, with all samples being analyzed within one minute of activation.
C.2. References


Table C.1: Water quality sampling and pilot performance monitoring for biofilm potential

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sampling/Monitoring frequency</th>
<th>Method</th>
</tr>
</thead>
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<tr>
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<tr>
<td>Hydrogen peroxide</td>
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<td>K$_2$[TiO(C$_2$O$_4$)$_2$] spectrophotometric</td>
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<tr>
<td>Flows</td>
<td>Three times per day</td>
<td></td>
</tr>
<tr>
<td>Reactor UV intensity</td>
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<td>UV dose (MP)</td>
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</tr>
<tr>
<td>Lamps on/off &amp; run hours</td>
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1. APHS *Standard Methods for Examination of Water and Wastewater*. 

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Appendix D

Bench-Scale UV/H$_2$O$_2$ Trihalomethane Formation Potential Tests
Bench-Scale UV/H₂O₂ Trihalomethane Formation Potential Tests

D.1 Methods

In order to investigate the effect of quenching hydrogen peroxide by chlorine and laboratory bench tests were performed. In the bench tests UV irradiation was accomplished by quasi-collimated beam systems in gently-stirred petri dishes (70x50 mm). The bench unit was built at GCWW based on the work of Bolton and Linden (2003). The unit contained four 15 W low pressure UV lamps emitting a monochromatic output of 253.7 nm through a four inch circular aperture. Irradiance was measured at the water surface by a 1400-A International Light Technology (ILT) radiometer equipped with a calibrated ILT detector with a NS254 filter and a TD #29022 diffuser. UV dose (fluence) was calculated by accounting for a variety of surface factors (surface reflection, sample depth, UV transmittance and petri factor) based on Beer’s Law (Bolton and Linden, 2003).

D.2 Results

The investigators performed bench-scale experiments to determine the effect of LP UV/H₂O₂ irradiation on chlorine quenched samples. Five replicate samples of CONV and Post-GAC water were dosed with 10 mg/L H₂O₂ and irradiated at pilot plant doses (900 mJ/cm² for the CONV water and 800 mJ/cm² for post-GAC water). Five replicate samples of CONV and Post-GAC were dosed with 10 mg/L H₂O₂ but not irradiated. The H₂O₂ residual was determined and the chlorine was added to partially quench the H₂O₂, so that a residual of 0.2 to 0.6 mg/L H₂O₂ remained. The samples were immediately placed in vials containing sodium thiosulfate. The results of these experiments are
presented in Table D.1. Very low levels of THMs were formed immediately, even though a small residual of H₂O₂ remained after chlorine quenching. Less instantaneous formation was observed in the Post-GAC water than in the CONV water and less formation was observed in the samples not exposed to UV than in the samples that had been exposed to UV. These values were compared to the TTHM 3-day SDS pilot values taken during that time period and the instantaneous formation was observed to be very small percentage of the TTHM 3-day SDS formation. (See Table D.1.) These results indicated that some fast acting DBP precursors were present in the non-irradiated waters, but that additional fast acting DBP precursors were formed through the UV/H₂O₂ process.

Using a sample of RMTP CONV water treated with 1000 mJ/cm² LPUV with 10 mg/L H₂O₂, Dotson and colleagues (2010) found that when hydrogen peroxide was partially quenched with chlorine, THMs increased as chlorine addition increased. Even though the reaction between free chlorine and hydrogen peroxide is fast, NOM appeared to compete with the hydrogen peroxide for the chlorine thus forming THMs. The THMs formed during the hydrogen peroxide quenching reaction were estimated to account for 9.4% of the total THMs measured when enough chlorine was added to achieve a 1 mg/L free chlorine residual after 24 hours. The results of this present study indicate that some of these newly formed precursors react very quickly with chlorine, although the TTHM formation attributed to chlorine quenching (with 0.2 to 0.6 residual H₂O₂) was a very small percentage of the total formation after the three day hold.
Table D.1: LP Collimated Beam & LP Pilot TTHM Comparison for Effect of UV/H₂O₂ and Chlorine Quenching

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<tr>
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<th>CONV with H₂O₂</th>
<th>Post-GAC with H₂O₂</th>
<th>CONV with UV/H₂O₂</th>
<th>Post-GAC with UV/H₂O₂</th>
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<tr>
<td>Inst. TTHMS - no Cl₂ residual</td>
<td>7.4 µg/L</td>
<td>1.2 µg/L</td>
<td>10.4 µg/L</td>
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<td>3-day TTHM SDS</td>
<td>150 µg/L</td>
<td>58 µg/L</td>
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<td>Inst. % of 3-day SDS TTHM</td>
<td>4.9%</td>
<td>2.1%</td>
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Table D.2: Water quality sampling protocol and pilot performance monitoring

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D.3 References


