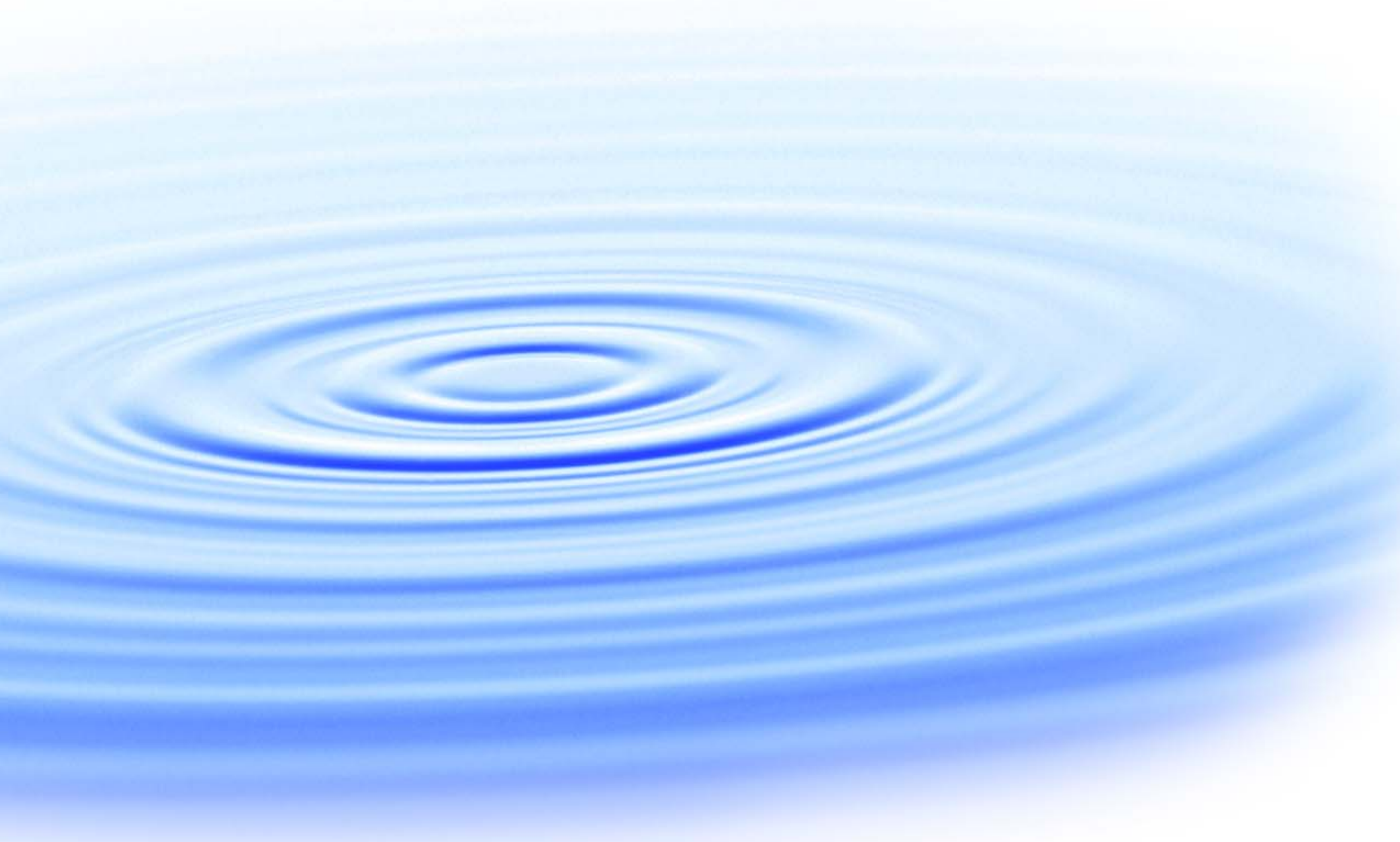
WATEREUSE FOUNDATION

Reaction Rates and Mechanisms of Advanced Oxidation Processes for Water Reuse



Reaction Rates and Mechanisms of Advanced Oxidation Processes (AOPs) for Water Reuse

About the WateReuse Foundation

The mission of the WateReuse Foundation is to conduct and promote applied research on the reclamation, recycling, reuse, and desalination of water. The Foundation's research advances the science of water reuse and supports communities across the United States and abroad in their efforts to create new sources of high quality water through reclamation, recycling, reuse, and desalination while protecting public health and the environment.

The Foundation sponsors research on all aspects of water reuse, including emerging chemical contaminants, microbiological agents, treatment technologies, salinity management and desalination, public perception and acceptance, economics, and marketing. The Foundation's research informs the public of the safety of reclaimed water and provides water professionals with the tools and knowledge to meet their commitment of increasing reliability and quality.

The Foundation's funding partners include the Bureau of Reclamation, the California State Water Resources Control Board, the Southwest Florida Water Management District, the California Energy Commission, and the California Department of Water Resources. Funding is also provided by the Foundation's Subscribers, water and wastewater agencies, and other interested organizations.

Reaction Rates and Mechanisms of Advanced Oxidation Processes (AOPs) for Water Reuse

William J. Cooper
University of California, Irvine

Shane A. Snyder
Southern Nevada Water Authority

Stephen P. Mezyk
California State University at Long Beach

Julie R. Peller
Indiana University Northwest

Michael G. Nickelsen
Haley & Aldrich

Cosponsors

Bureau of Reclamation
State Water Resources Control Board, CA

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For more information, contact:
WateReuse Foundation
1199 North Fairfax Street, Suite 410
Alexandria, VA 22314
703-548-0880
703-548-5085 (fax)
www.WateReuse.org/Foundation

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Abbreviations

ADDA	3-Amino-9-methoxy-2,6,8-trimethyl-10-phenyl-4,6-dienoic acid
AOP	Advanced oxidation process
AO/RP	Advanced oxidation/reduction process
BMF	Before membrane filtration (in wastewater treatment)
BPA	Bisphenol A
CO_3^{2-}	Carbonate ion
CSULB	California State University at Long Beach
DI	Deionized water
DBP	Disinfection by-products
DEET	*N,N*-diethyl-*meta*-toluamide
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EDRs	Endocrine disruptors
EfOM	Effluent organic matter
EPOCs	Emerging pollutants of concern
GC/MS	Gas chromatography/mass spectrometry
H•	Hydrogen atom
•OH	Hydroxyl radical
HCO_3^-	Bicarbonate ion
HPLC	High-performance liquid chromatography
HPLC/PDA	High-performance liquid chromatography/photodiode array detection
IUN	Indiana University Northwest
LC/MS	Liquid chromatography/mass spectrometry
LINAC	Linear accelerator
MFE	Microfiltration effluent
$mg\ L^{-1}$	Milligrams per liter
ND	Not detected
NDMA	*N*-Nitrosodimethylamine
$ng\ L^{-1}$	Nanograms per liter
PAC	Project Advisory Committee
PCP	Personal care product
PI	Principal investigator
e^-_{aq}	Solvated electron
Q1	Secondary treated wastewater from Orange County Sanitary District
ROP	Reverse osmosis product water
SNWA	Southern Nevada Water Authority
SRFA	Suwannee River fulvic acid
TOC	Total organic carbon

μg/L	Micrograms per liter
UC	University of California
UNCW	University of North Carolina–Wilmington
UV	Ultraviolet
UVP	Ultraviolet product water
WRF	WateReuse Foundation
WWTP	Wastewater treatment plant

FOREWORD

The WateReuse Foundation, a nonprofit corporation, sponsors research that advances the science of water reclamation, recycling, reuse, and desalination. The Foundation funds projects that meet the water reuse and desalination research needs of water and wastewater agencies and the public. The goal of the Foundation's research is to ensure that water reuse and desalination projects provide high-quality water, protect public health, and improve the environment.

A Research Plan guides the Foundation's research program. Under the plan, a research agenda of high-priority topics is maintained. The agenda is developed in cooperation with the water reuse and desalination communities including water professionals, academics, and Foundation Subscribers. The Foundation's research focuses on a broad range of water reuse research topics including:

- Defining and addressing emerging contaminants;
- Public perceptions of the benefits and risks of water reuse;
- Management practices related to indirect potable reuse;
- Groundwater recharge and aquifer storage and recovery;
- Evaluation and methods for managing salinity and desalination; and
- Economics and marketing of water reuse.

The Research Plan outlines the role of the Foundation's Research Advisory Committee (RAC), Project Advisory Committees (PACs), and Foundation staff. The RAC sets priorities, recommends projects for funding, and provides advice and recommendations on the Foundation's research agenda and other related efforts. PACs are convened for each project and provide technical review and oversight. The Foundation's RAC and PACs consist of experts in their fields and provide the Foundation with an independent review, which ensures the credibility of the Foundation's research results. The Foundation's Project Managers facilitate the efforts of the RAC and PACs and provide overall management of projects.

The Foundation's primary funding partners include the Bureau of Reclamation, California State Water Resources Control Board, the Southwest Florida Water Management District, the California Energy Commission, Foundation Subscribers, water and wastewater agencies, and other interested organizations. The Foundation leverages its financial and intellectual capital through these partnerships and funding relationships.

The field of water reuse has seen great strides with multiple benefits in the application of new techniques and technologies, and these will continue to evolve as additional processes are found and new contamination problems are identified that require nontraditional solutions. The main objective of this study was to develop a better understanding of the water-based free radical chemistry in the destruction of organic microconstituents. The long-term goal of research of this nature is to provide the data necessary to develop kinetic models that describe the underlying chemistry for advanced oxidation process applications.

David L. Moore	**G. Wade Miller**
Chair	Executive Director
WateReuse Foundation	WateReuse Foundation

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Principal Investigator

William J. Cooper, Director and Professor, Urban Water Research Center and Civil and Environmental Engineering, University of California, Irvine, CA

Co-Investigators

Shane A. Snyder, R&D Project Manager, Applied R&D Center, Southern Nevada Water Authority, Las Vegas, NV

Stephen P. Mezyk, Professor, California State University at Long Beach, Long Beach, CA

Julie R. Peller, Associate Professor, Indiana University Northwest, Gary, IN

Michael G. Nickelsen, Senior Scientist, Haley & Aldrich of New York, Rochester, NY

Project Advisory Committee

Greg G. Bradshaw, HDR Engineering, Inc.

Joseph Cotruvo, Ph.D., Joseph Cotruvo & Associates LLC

Saied Delagah, Bureau of Reclamation

Kenneth P. Ishida, Ph.D., Orange County Water District

Richard A. Mills, California State Water Resources Control Board

Samuel L. Mowbray, Ph.D., Orange County Sanitation District

Participating Agencies

Orange County (Florida) Utilities Water Division, Orlando, FL

Southern Nevada Water Authority, Las Vegas, NV

Collaborating Personnel

S. Kirk Cole, Ph.D., P.E., McKim & Creed, Virginia Beach, VA

Florian Follut, Ph.D. student, Laboratoire Chimie de l'Eau et de l'Environnement, Ecole Supérieure d'Ingénieurs de Poitiers

Jinyoung Jung, Ph.D., Senior Research Scientist, Center for Environmental Technology Research, Korea Institute of Science and Technology

Joonseon Jeong, Ph.D., Department of Civil and Environmental Engineering, University of California, Irvine, CA

Kimberly Kunihiro, Orange County (Florida) Utilities Water Division, Orlando, FL

Weihua Song, Department of Civil and Environmental Engineering, University of California, Irvine, CA

EXECUTIVE SUMMARY

PROJECT OVERVIEW AND HISTORY

In January 2006, the WateReuse Foundation (WRF) issued project funding agreement WRF-04-017 with the University of North Carolina, Wilmington (UNCW), in partnership with the Southern Nevada Water Authority (SNWA), California State University at Long Beach (CSULB), Indiana University Northwest (IUN), Orange County (Florida) Water Utilities, the Urban Water Research Center at the Henry Samueli School of Engineering at UC Irvine, and McKim & Creed and Haley & Aldrich, to complete a study titled *Reaction Rates and Mechanisms of Advanced Oxidation Processes (AOPs) for Water Reuse*.

In July 2006, Principal Investigator (PI) William Cooper left UNCW and assumed responsibilities as the director of the Urban Water Research Center and professor of civil and environmental engineering at the Henry Samueli School of Engineering at UC Irvine. The availability of a well-equipped mass spectrometer laboratory (user facility) at UC Irvine allowed the project team to greatly expand the scope of work. This expansion resulted in the ability to determine many more chemical compound destruction pathways than originally planned.

OBJECTIVES

The main objective of this study was to develop a better understanding of the water-based free radical chemistry in the destruction of organic microconstituents by:

- Determining reaction rates of 30 to 50 target chemicals with hydroxyl radicals, $^{\bullet}OH$, and hydrated electrons, e^{-}_{aq}.

While it is relatively straightforward to determine bimolecular reaction rates using standard techniques of radiation chemistry, it is very time-consuming to determine full, detailed destruction mechanisms for this many compounds. Therefore, we also proposed:

- Elucidating destruction mechanisms for five selected target compounds representative of broader classes of organic microconstituents.

The third major objective expands the scope of work to include studies in waters of different quality:

- Determining the efficiency of the hydroxyl radical-mediated destruction of bisphenol A and three other model organic contaminants, in pure water, laboratory solutions containing bicarbonate ion and/or dissolved organic matter, and treated wastewaters of different quality.

The long-term goal of research of this nature is to provide the data necessary to develop kinetic models that describe the underlying chemistry for advanced oxidation process applications.

PROJECT SUMMARY AND CONCLUSIONS

Radiation chemistry allows the clean, quantitative formation of radicals and is the most versatile approach for studying the fundamental free radical chemistry of chemical contaminants of interest in water reuse. The main conclusions of this project are:

- Measured reaction rate constants with the hydroxyl radical for the 51 compounds studied were in the range of 1×10^9 to 10×10^9 M^{-1} s^{-1} with few exceptions (see Table E.1). A reaction rate constant in this range suggests that the compound of concern has a high probability of being effectively destroyed by an advanced oxidation process radical.

- The absolute reaction rate constants with the solvated electron (e^-_{aq}), with few exceptions, fall in the range of 10^8 to 10^{10} M^{-1} s^{-1}. Although this range was broader than that for the hydroxyl radical, these results also suggest that advanced reduction processes that produce reducing radicals are similarly capable of organic contaminant destruction.

- Radical reaction efficiency is also a critically important parameter when one is considering the application of advanced oxidation free radical processes to water reuse. This efficiency parameter evaluates the effectiveness of the reactive species in the destruction of chemical contaminants, which varies according to water quality. In pure water, the hydroxyl radical reacts with most organic contaminants with less than 100% efficiency. A decrease in the $^{\bullet}OH$ and contaminant reaction occurs in the presence of radical scavengers, which is dependent on many factors, including the nature and/or concentration of dissolved species, efficiency of $^{\bullet}OH$ reaction with contaminants in pure water, and other effects potentially present with additional dissolved species.

- Studies that were based on liquid chromatography/mass spectrometry (LC/MS) measurements were conducted to elucidate reaction by-products of the free radical-induced contaminant degradation reactions. In many cases, several reaction by-products potentially fit the measured MS values. This situation has led to many proposed destruction mechanisms for the compounds studied. With the exception of the sulfa drugs listed in Table E.1, destruction mechanisms for all of these compounds were outlined. Reaction by-products were not chemically synthesized or isolated for further study.

Table E.1. Summary of Reaction Rate Constants Determined in This Study

Group	Compound	Reaction Rates		Reference
		$^{\bullet}$OH (M^{-1} s^{-1})	e^{-}_{aq} (M^{-1} s^{-1})	
Lipid regulators	Clofibric acid	$(6.98 \pm 0.12) \times 10^{9}$	$(6.59 \pm 0.43) \times 10^{8}$	Razavi et al., 2009
	Bezafibrate	$(8.00 \pm 0.22) \times 10^{9}$	$(1.12 \pm 0.03) \times 10^{10}$	
	Gemfibrozil	$(10.0 \pm 0.60) \times 10^{9}$	$(6.26 \pm 0.58) \times 10^{8}$	
Antibiotics	Tetracycline	$(6.34 \pm 0.11) \times 10^{9}$	$(2.16 \pm 0.08) \times 10^{10}$	Manuscript in preparation
	Chlortetracycline	$(5.20 \pm 0.23) \times 10^{9}$	$(1.32 \pm 0.18) \times 10^{10}$	
	Oxytetracycline	$(5.63 \pm 0.03) \times 10^{9}$	$(2.32 \pm 0.05) \times 10^{10}$	
	Doxycycline	$(7.58 \pm 0.12) \times 10^{9}$	$(2.52 \pm 0.02) \times 10^{10}$	
Insect repellent	DEET	$(4.95 \pm 0.18) \times 10^{9}$	$(1.34 \pm 0.04) \times 10^{9}$	Song et. al., 2009a
ß-blockers	Atenolol	$(7.05 \pm 0.27) \times 10^{9}$	$(5.91 \pm 0.21) \times 10^{8}$	Song et. al., 2008b
	Metoprolol	$(8.39 \pm 0.06) \times 10^{9}$	$(1.73 \pm 0.03) \times 10^{8}$	
	Propranolol	$(1.07 \pm 0.02) \times 10^{10}$	$(1.26 \pm 0.02) \times 10^{10}$	
ß-lactam antibiotics	Penicillin G	$(7.97 \pm 0.11) \times 10^{9}$	$(3.92 \pm 0.10) \times 10^{9}$	Song et. al., 2008a
	Penicillin V	$(8.76 \pm 0.28) \times 10^{9}$	$(5.76 \pm 0.24) \times 10^{9}$	
	Amoxicillin	$(6.94 \pm 0.44) \times 10^{9}$	$(3.47 \pm 0.07) \times 10^{9}$	
	(+)-6-aminopenicillanic acid	$(2.40 \pm 0.05) \times 10^{9}$	$(3.35 \pm 0.06) \times 10^{9}$	
Fluoro-quinolones	Levofloxacin	$(7.60 \pm 0.17) \times 10^{9}$	$(2.46 \pm 0.05) \times 10^{10}$	Santoke et al., 2009
	Lomefloxacin	$(8.04 \pm 0.62) \times 10^{9}$	$(2.79 \pm 0.05) \times 10^{10}$	
	Norfloxacin	$(6.61 \pm 0.18) \times 10^{9}$	$(2.18 \pm 0.10) \times 10^{10}$	
	Orbifloxacin	$(6.94 \pm 0.08) \times 10^{9}$	$(2.25 \pm 0.02) \times 10^{10}$	
	Flumequine	$(8.26 \pm 0.28) \times 10^{9}$	$(1.83 \pm 0.01) \times 10^{10}$	
	Marbofloxacin	$(9.03 \pm 0.39) \times 10^{9}$	$(2.41 \pm 0.02) \times 10^{10}$	
	Danofloxacin	$(6.15 \pm 0.11) \times 10^{9}$	$(1.68 \pm 0.02) \times 10^{10}$	
	Enrofloxacin	$(7.95 \pm 0.23) \times 10^{9}$	$(1.89 \pm 0.02) \times 10^{10}$	
	6-Fluoro-4-oxo-1,4-dihydro-3-quinoline	$(7.65 \pm 0.20) \times 10^{9}$	$(1.49 \pm 0.01) \times 10^{10}$	
Antibiotic	Trimethoprim	$(8.34 \pm 0.47) \times 10^{9}$	$(1.36 \pm 0.01) \times 10^{10}$	Manuscript in preparation
Atrazine	Atrazine	$(3.17 \pm 0.18) \times 10^{9}$	$(1.40 \pm 0.10) \times 10^{10}$	Manuscript in preparation
	Atrazine-desisopropyl	$(1.94 \pm 0.07) \times 10^{9}$	$(9.17 \pm 0.23) \times 10^{9}$	
	Atrazine-desethyl	$(1.20 \pm 0.04) \times 10^{9}$	$(9.63 \pm 0.35) \times 10^{9}$	
	Atrazine-6-chloro-desethyl-desisopropyl	$(8.23 \pm 0.81) \times 10^{7}$	$(1.31 \pm 0.04) \times 10^{10}$	
	Atrazine-6-ol-desethyl-desisopropyl	$(1.94 \pm 0.14) \times 10^{8}$	$(9.27 \pm 0.15) \times 10^{9}$	
	Cyanuric acid	$< 10^{7}$	$(2.23 \pm 0.10) \times 10^{9}$	
Nonsteroidal anti-inflammatory	Diclofenac	$(9.29 \pm 0.11) \times 10^{9}$	$(1.53 \pm 0.03) \times 10^{9}$	Manuscript in preparation
	Ibuprofen	$(5.97 \pm 0.22) \times 10^{9}$	$(4.76 \pm 0.18) \times 10^{8}$	
	Naproxen	$(7.53 \pm 0.26) \times 10^{9}$	$(2.43 \pm 0.13) \times 10^{9}$	

Table E.1. Summary of Reaction Rate Constants Determined in This Study (Continued)

Harmful algal toxins	Domoic acid	(9.45 ± 0.035) × 10^9	ND	Jones et al., 2009
	Kainic acid	(2.46 ± 0.029) × 10^9	ND	
	Microcystin-LR	(2.3 ± 0.1) × 10^{10}	ND	Song et al., 2009b
Sulfa drugs	Sulfamethazine	(8.3 ± 0.8) × 10^9	(2.4 ± 0.1) × 10^{10}	Mezyk et al., 2007
	Sulfamethizole	(7.9 ± 0.4) × 10^9	(2.0 ± 0.1) × 10^{10}	
	Sulfamethoxazole	(8.5 ± 0.3) × 10^9	(1.0 ± 0.03) × 10^{10}	
	Sulfamerazine	(7.8 ± 0.3) × 10^9	(2.0 ± 0.05) × 10^{10}	
X-ray contrast compounds	Diatrizoate	(0.96 ± 0.02) × 10^9	(2.13 ± 0.03) × 10^{10}	Manuscript in preparation
	Iohexol	(3.21 ± 0.13) × 10^9	(3.35 ± 0.03) × 10^{10}	
	Iopromide	(3.34 ± 0.14) × 10^9	(3.25 ± 0.05) × 10^{10}	
	Iopamidol	(3.42 ± 0.28) × 10^9	(3.37 ± 0.05) × 10^{10}	
	Iomeprol	(2.03 ± 0.13) × 10^9	(3.47 ± 0.02) × 10^{10}	
	3,5-*bis*(acetamino) benzoic acid	6.0 × 10^9	4.9 × 10^9	
	2,3,5-Triodbenzoic acid	9.7 × 10^9	2.5 × 10^{10}	
	3-acetamino benzoic acid	5.4 × 10^9	3.8 × 10^9	
	Acetanilide	ND	5.0 × 10^8	
Bisphenol A	Bisphenol A	(6.9± 0.2) × 10^9		Peller et al., 2009
Suwannee River, Saguaro Lake, and effluent organic matter fractions	Suwannee River fulvic acid	(1.39 ± 0.16) × 10^8	ND	Westerhoff et al., 2007
	Suwannee River fulvic acid	(1.87 ± 0.07) × 10^8	ND	
	Suwannee River fulvic acid	(1.55 ± 0.04) × 10^8	ND	
	Saguaro Lake hydrophobic acid	(1.73 ± 0.04) × 10^8	ND	
	Saguaro Lake hydrophilic acid	(1.45 ± 0.02) × 10^8	ND	
	Saguaro Lake hydrophobic neutral	(2.18 ± 0.13) × 10^8	ND	
	Nogales WWTP hydrophobic neutral	(1.72 ± 0.13) × 10^8	ND	
	Nogales WWTP transphilic neutral	(4.53 ± 0.54) × 10^8	ND	
	Nogales WWTP transphilic acid	(3.63 ± 0.31) × 10^8	ND	

[a] DEET, *N,N*-diethyl-*meta*-toluamide.

CHAPTER 1

INTRODUCTION

The field of water reuse has seen great strides with multiple benefits in the application of new techniques and technologies, and these will continue to evolve as additional processes are found and new contamination problems are identified that require nontraditional solutions. In particular, contaminant destruction technologies such as advanced oxidation and/or reduction processes (AO/RPs) will be recommended and implemented in many new plants and likely will be specified in upgrading existing plants.

1.1 LIMITATIONS OF TRADITIONAL WASTEWATER TREATMENT

Municipal wastewater treatment plants potentially offer an enormous supply of water for public reuse. The end use for such treated wastewater is most appealing for nonpotable purposes such as irrigation, industrial cooling, toilet flushing, and industrial cleaning and maintenance. Presently, the minimum municipal treatment established by the Clean Water Act requires primary and secondary levels of treatment, and most (~70%) of wastewater treatment plants in the United States comply only with this minimum requirement. While an effective primary/secondary treatment facility can result in the removal of up to 90% of dissolved organics, the remaining dissolved contaminant load is discharged into natural water reservoirs. This ideal scenario of 90% removal is not the norm, a truth reflected in studies reported from around the world that clearly establish the presence of multiple organic contaminants in the effluent of wastewater treatment plants (Clara et al., 2004; Glassmeyer et al., 2005; Khetan and Collins, 2007; Lishman et al., 2006; Loffler et al., 2005; Loyo-Rosales et al., 2007; Ternes, 1998).

Many municipal wastewater treatment plants are involved in, or considering, water reuse practices, which requires postsecondary treatment of wastewater. Guidelines and regulations for water reuse applications vary from state to state and depend on intended end use. According to a 2004 U.S. Environmental Protection Agency (EPA) document, nearly 2 billion gallons of treated wastewater was being reused daily in the country, with the goal in many states to dramatically increase this volume (*Guidelines,* 2004). Additional effective treatments of wastewater beyond the primary/secondary treatment requirement, which greatly reduce the dissolved organic contaminants, are therefore required. AO/RPs are appealing in that they destroy organic contaminants to the point of benign compounds or mineralization, unlike many of the established filtration or adsorption processes used in current advanced water treatment. It is important to consider and therefore ascertain all aspects of AO/RPs and their effectiveness in wastewater treatment.

The treatment of wastewaters containing low levels of organic contaminants is difficult, and advanced oxidation processes (AOPs) may be regarded as the best universal treatment option, because of the indiscriminate nature of the hydroxyl radical. The use of reducing radicals such as the hydrogen atom and hydrated electron remains less appealing because of their fast reaction with dissolved oxygen that is present in these wastewaters. However, many aspects of hydroxyl radical-mediated reactions are still unexplored.

1.2 AO/RPs

AOPs are defined as technologies that generate the reactive hydroxyl radical ($^{\bullet}$OH) in situ, which then reacts with contaminant compounds to reduce their concentrations. There are many ways to produce hydroxyl radicals in water. Common examples include the UV photolysis of hydrogen peroxide (H_2O_2/UV), the reaction of hydrogen peroxide with ozone (H_2O_2/O_3), and the photolysis of ozone (O_3/UV). These methods require adding relatively large amounts of reactive chemicals (namely, H_2O_2 and O_3) to the water under treatment and then using external energy (UV radiation) or chemistry to produce the $^{\bullet}$OH radical. Other methods for hydroxyl radical production include ionizing radiation techniques, TiO_2/UV, Fenton's reagent, high-frequency ultrasound, and various combinations of these techniques. While all of these methods have been studied in research settings, those presently used in water reuse are ozone with hydrogen peroxide (H_2O_2) and UV light with H_2O_2, because of economic and practical considerations.

Ozone, hydrogen peroxide, and UV light can also individually react with organic contaminants, depending on their structures. Therefore, complications may arise from the use of these methods, as these added chemicals or energy sources directly react with the organics of concern. For example, ozone readily oxidizes organic compounds that contain isolated double bonds. While the additional direct reaction may provide some synergistic contaminant removal on a large scale, it complicates the elucidation of the radical-induced degradation chemistry involved. The advantage of the radiation chemistry techniques incorporated in this study is that the utilization of ionizing radiation allows for the isolated study of radical chemistries. Furthermore, one of the major drawbacks of all these AOPs is that it is not a simple task to determine the absolute concentration of $^{\bullet}$OH in solution. Methods involving gamma rays or electron beams provide a simpler, direct way to decompose water itself into radicals through ionizing radiation. This process creates a clean solution of radicals with known absolute concentrations for the study of advanced oxidation/reduction chemistry.

Radiation chemistry is one of the most practical techniques for the study of both hydroxyl radical reactions and aqueous electron reactions in water solutions, since the data are readily translated to AO/RPs under real-world conditions (Mezyk et al., 2007; Peller et al., 2003a; Razavi et al., 2009; Tobien et al., 2000). As long as the concentrations of the dissolved solute species under investigation are relatively low (<0.1 M), the ionizing radiation initially affects only the water molecules and subsequently creates hydroxyl radicals and aqueous electrons (Buxton et al., 1988). The subsequent radical reactions with the added solute can then be studied in the presence or absence of oxygen, either as transient (nano- to microscale time) or steady-state (minutes to hours) experiments. In pure water solutions saturated with nitrous oxide gas, the only radical species formed is the hydroxyl radical. The chemistry that takes place is due only to this oxidant. Therefore, for efforts to understand the effects of the hydroxyl radical on water contaminants (AOPs), radiation chemistry techniques are exceptionally valuable.

The ability of the hydroxyl radical to react with organic contaminants is well documented (Acero et al., 2000; Huber et al., 2003; Oppenlander, 2003), and with sufficient reaction time, the ultimate breakdown products of AOPs are CO_2 and water and related inorganic ions (Peller et al., 2003b; Ruppert and Bauer, 1994; Sun, 1993; Vinodgopal, 1998). To date, the vast majority of AOP studies have involved organic compounds dissolved in high-quality deionized water. However, the efficiency of the hydroxyl radical with water contaminants in "real water" solutions depends on many additional factors. In the context of water reuse, the water quality is a significant factor and therefore was the main focus of project objective three.

In order to determine the effectiveness and efficiency of the hydroxyl radical (or aqueous electron) reaction with organic contaminants, the rates of these reactions need to be determined, in addition to the rates of reaction of all potential scavengers. However, while rate constant comparisons can be useful for computer modeling of AO/RP water treatment systems, the chemical processes can be much more complex and additional chemistry must often be considered. Hydroxyl radical and hydrated electron reactions are also especially known for promoting the formation of new radicals or subsequent radical reactions. For example, in the presence of carbonate/bicarbonate ions (present in all natural water matrices), the hydroxyl radical propagation often creates a different oxidant, the carbonate radical anion, whose significance is dictated by the concentration of the dissolved ion species and the solution pH (Behar et al., 1970; Mazellier et al., 2007). To quantitatively account for this additional chemistry, any research in advanced oxidation chemistry (promoted by hydroxyl radical reactions) as it applies to real water systems must involve real water solutions or laboratory solutions that more closely mimic or model real waters. The work reported from this study provides an extensive study of hydroxyl radical rate constants and data from a vast array of experiments conducted in both treated wastewaters and laboratory model solutions.

1.3 MODEL COMPOUNDS

The model compounds chosen in this project were determined through several important considerations. First, the input from the project advisory committee (PAC) was crucial as our PAC members had practical insights into many of the problematic compounds found in wastewater and treated wastewater. Second, groups of emerging pollutants of concern (EPOCs), endocrine disruptors (EDRs), or personal care products (PCPs) are microcontaminants of a more universal concern and are therefore good candidates for model chemicals. Selection considerations for this class included level of usage, biological activity, and chemical similarities. Many have been detected and reported in several published studies: for example, caffeine, ibuprofen, sulfamethoxazole, atenolol, etc. (Khetan and Collins, 2007; Kolpin et al., 2002; Kolpin et al., 1996; Wert et al., 2007).

The third major consideration involved in compound selection for this study was experimental feasibility. The model compounds needed to be somewhat soluble in water, and detectable by HPLC/PDA (high-performance liquid chromatography/photodiode array detection). Water solubility was required mainly because of the minimum solute concentrations necessitated by the radiolysis experiments. At the Radiation Laboratory, University of Notre Dame, three steady-state irradiation sources with radical generation rates of ~2 to 50 μM per min were available to us. The level of radiation emitted from these sources is very difficult to experimentally modify, and we eventually determined that the lowest possible concentration for our established experimental procedure was approximately 30 μM.

In the early portion of this project, 0.5 mM solutions were used. Once these preliminary experiments were performed to establish the experimental procedures and efficiency data, our goal was to better mimic real wastewater concentrations. These solute concentrations were lowered to approximately 50 μM, the target concentrations of most of the experiments performed in the last 18 months of the project. For these lower-concentration solutions, only the lowest-dose gamma source was useful.

Prior to the formal starting date of the project and to the first meeting with the PAC, experiments were conducted using the high-profile contaminant bisphenol A (BPA), which is used in the manufacture of certain polycarbonate plastics. The structure of BPA consists of two phenolic rings, a very common structural moiety present in an extensive number of organic contaminants. Also, BPA is classified as an EDR and has been detected in many natural water basins (Fromme et al., 2002; Suzuki et al., 2004). With this established experimental base already in place, BPA was utilized as a model compound throughout the study.

Sulfa drug antibiotics were the next class of contaminants studied. The hydroxyl radical and hydrated electron reaction rate constants of four different sulfa drugs were determined (Table E.1). These experiments were followed up with steady-state hydroxyl radical and aqueous electron-promoted degradations (Mezyk et al., 2007) to establish reaction efficiencies and elucidate the reaction mechanisms for both of these radicals. The conclusions from these experiments led to the definition of the *removal constant* and a better understanding of conditions necessary to determine *removal efficiencies*.

Based on the findings of these two sets of experiments, we expanded our investigations to a diverse range of compounds, as noted in Table E.1. Studied model compounds ranged from atrazine to antibiotics and from β-blockers to algal toxins. It was straightforward to measure these kinetic parameters using high-quality deionized water, and it is especially important that these rate constants remain the same no matter the level of water quality. A much shorter list of compounds was studied by using the characterized treated wastewater and laboratory solution matrices in the steady-state gamma radiolysis experiments. In addition to BPA, sulfamethazine, caffeine, and *N,N*-diethyl-*meta*-toluamide (DEET) were utilized as model compounds in real-world waters.

CHAPTER 2

EXPERIMENTAL METHODS AND RESEARCH APPROACH

2.1 RADIOLYSIS CHEMISTRY

AO/RPs are characterized by their generation of radicals in water that react with and destroy organic contaminants. Most AOPs typically generate the oxidizing hydroxyl radical, $^{\bullet}OH$, but other processes can create reducing species such as hydrated electrons, e_{aq}^{-}, or hydrogen atoms, $H^{\bullet}$.

While many laboratory approaches can be used to generate hydroxyl radicals, hydrated electrons, and hydrogen atoms, we chose electron pulse radiolysis, which uses short pulses of high-energy electrons (from a linear accelerator), and continuous gamma irradiation from radioactive ^{60}Co or ^{137}Cs sources as our techniques for this study. For both methods, the initial high-energy irradiation of a solution causes direct ionization of the water molecules yielding free electrons that subsequently become hydrated, e^{-}_{aq}, and H_2O^{+} ions, which decompose to give the hydroxyl radicals, $^{\bullet}OH$ and H^{+}. The subsequent reactions of these initially formed species include formation of H_2O_2 (from the combination of two $^{\bullet}OH$ radicals), $^{\bullet}H$ (from e^{-}_{aq} and H^{+}), and H_2 (from the reaction of two $^{\bullet}H$ atoms). Radiolysis techniques have been used for over 50 years in the field of radiation chemistry, and it has been quantitatively established that the degradation species produced in water (pH 3 to 11) are constant. They are given by Buxton et al. (1988):

$$H_2O \rightsquigarrow e^{-}_{aq}\,(2.7) + H^{\bullet}\,(0.6) + {}^{\bullet}OH\,(2.8) + H_2\,(0.5) + H_2O_2\,(0.7) + H^{+}\,(2.7) \qquad [2\text{-}1]$$

$$H_2O \rightsquigarrow e^{-}_{aq}\,(0.27) + H^{\bullet}\,(0.06) + {}^{\bullet}OH\,(0.28) + H_2\,(0.05) + H_2O_2\,(0.07) + H^{+}\,(0.27) \qquad [2\text{-}2]$$

The values in parentheses are the yields of each species produced. There are two conventions that have been used in the field of radiation chemistry. Equation 2-1 relates absorbed energy in electronvolts (eV) to the absolute number of molecules formed. By convention, for a 100-eV absorbed dose, there will be 2.6 solvated electrons (e^{-}_{aq}) formed. In Equation 2-2, the yields are given in micromoles per joule (J) of absorbed dose. The absorbed dose in pulse radiolysis is determined by using dosimetry (Buxton and Stuart, 1995) which was performed with N_2O-saturated, 1.00×10^{-2} M KSCN solutions at $\lambda = 472$ nm ($G_{\varepsilon} = 5.2 \times 10^{-4}\ m^2\ J^{-1}$) with average doses of 3 to 5 Gy per 2- to 3-ns pulse.

The major advantage of using techniques that have been developed in radiation chemistry is that they provide easy access for the simultaneous, quantitative generation of three reactive species found in AOPs with concentrations in the nanomolar-to-micromolar range: $^{\bullet}OH$, $H^{\bullet}$, and e^{-}_{aq}. The H_2 and H^{+} produced are not reactive, and H_2O_2 is reactive only at much longer times.

To evaluate the rate constant for the reaction with only one of these radical species with a chemical contaminant, the radical species can be isolated by adjusting the experimental conditions of the solution. For example, in this work the reaction of the oxidizing $^{\bullet}OH$ radical was studied in nitrous oxide (N_2O)-saturated solutions, while the other two radicals, e^{-}_{aq} and $^{\bullet}H$, were converted to $^{\bullet}OH$ via the following fast reactions (Buxton et al., 1988):

$e^-_{aq} + N_2O + H_2O \rightarrow {}^\bullet OH + OH^- + N_2 \quad k_{2\text{-}3} = 9.1 \times 10^9\ M^{-1}\ s^{-1}$ [2-3]
${}^\bullet H + N_2O \rightarrow {}^\bullet OH + N_2 \quad k_{2\text{-}4} = 2.1 \times 10^6\ M^{-1}\ s^{-1}$ [2-4]

The use of N_2O effectively doubles the yield of hydroxyl radicals in the system.

To study only the reactions of e^-_{aq}, water solutions were presaturated with nitrogen gas and had 0.1 M isopropanol added. This alcohol scavenged the initially formed hydroxyl radicals and hydrogen atoms, according to the following equations:

$(CH_3)_2CHOH + {}^\bullet OH \rightarrow (CH_3)_2C^\bullet OH + H_2O \quad k_{2\text{-}5} = 1.9 \times 10^9\ M^{-1}\ s^{-1}$ [2-5]
$(CH_3)_2CHOH + {}^\bullet H \rightarrow (CH_3)_2C^\bullet OH + H_2 \quad k_{2\text{-}6} = 7.4 \times 10^7\ M^{-1}\ s^{-1}$ [2-6]

The product alcohol radical, $(CH_3)_2C^\bullet OH$, is relatively inert and will not usually interfere with the reductive chemistry of interest.

Hydrogen atoms can be isolated by making the solutions acidic in the presence of an alcohol so that the formed hydrated electrons preferentially react with the acid present:

$e^-_{aq} + H^+ \rightarrow {}^\bullet H$ [2-7]

Then the ${}^\bullet OH$ radical again reacts with the added alcohol. While hydrogen atoms also react with the added alcohol, they do so much more slowly than the hydroxyl radicals (usually by about a factor of 1000); therefore, if one selects the chemical concentrations carefully, hydrogen atoms will preferentially undergo reactions with the added chemical of concern. If the acidic conditions are incompatible with the contaminant chemicals, then electron-paramagnetic-resonance (EPR) absorption studies can be utilized in a neutral-pH solution (Bartels and Mezyk, 1993; Fessenden and Verma, 1977). However, in this study we did not evaluate any ${}^\bullet H$ atom chemistry.

2.2 ELECTRON PULSE RADIOLYSIS

2.2.1 General Experimental Conditions

The experimental setup utilized a continuous-flow system, so that an unirradiated solution was continually presented to the pulsed electron beam, as shown in Figure 2.1.

For our experiments, the solutions were continuously sparged in their sample vessels. As none of the chemicals for this study were volatile, this arrangement did not affect their concentrations.

The radical reactions induced by the electron irradiation were monitored using UV/visible absorption spectroscopy. The probe light was generated by a pulsed 1000-W Xe lamp and detected by a monochromator/photomultiplier tube system (Figure 2.2).

2.2.2 Evaluation of ${}^\bullet$OH Reaction Rate Constants using Transient Absorption Spectroscopy

The very weak absorption at far-UV wavelengths of the hydroxyl radical prevents direct monitoring of its real-time disappearance. Instead, the rate of appearance of the oxidized chemical transient species is usually monitored. For example, one group of compounds that were studied included tetracycline (Figure 2.3).

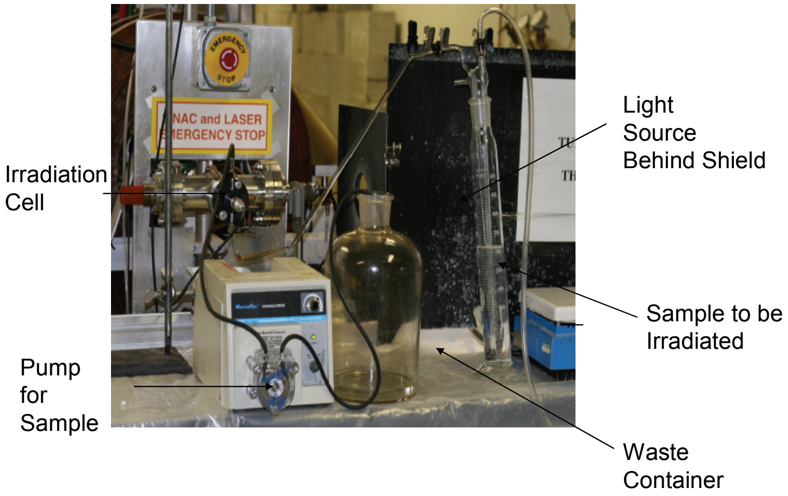


Figure 2.1. Photograph of experimental setup used for pulse radiolysis experiments in this study. (Note: Sample solution was continuously pumped through the irradiation cell to insure that unreacted compound was in the cell for each pulse.)

Figure 2.2. Transient absorption spectrometer.

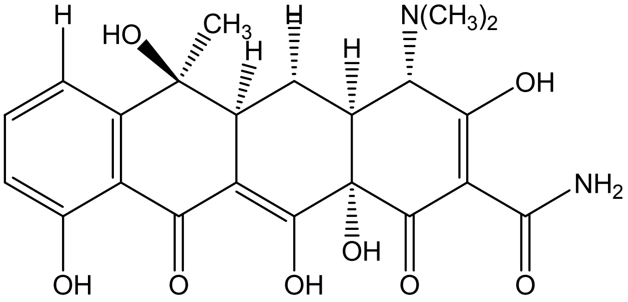


Figure 2.3. Chemical structure of tetracycline.

Upon pulsed electron irradiation in N_2O-saturated solution, the initially formed hydroxyl radicals react with the dissolved tetracycline to give a transient species that has a significant absorption over the wavelength range of 400 to 550 nm. These absorption spectra are given in Figure 2.4 for different times up to 400 μs. Because of the strong self-absorption of tetracycline below 400 nm, transient spectra could not be recorded at lower wavelengths.

One purpose of recording the transient spectra is to provide information on the mechanism of the free-radical chemistries of the compounds. The $^{\bullet}OH$ reaction preferentially adds to the electron-rich aromatic ring, as evidenced by how the transient absorption spectra observed are red-shifted by 50 nm compared to the absorption maximum of the parent compound (Sharma et al., 1997). The molar absorptivity at the λ_{max} (ε_{max}) for the tetracycline transient was obtained by using a *G* value of 0.59 μmol J^{-1} (total $^{\bullet}OH$ yield in N_2O-saturated water) at the maximum absorbance and is also listed in Table 2.1.

Once the transient absorption spectra were recorded, the wavelength for evaluating the reaction rate constant was determined. For tetracycline, the peak at 430 nm was chosen and then the transient time profile for solutions of various tetracycline concentrations was obtained (Figure 2.5a). In general, all of the kinetic data were determined by averaging 8 to 12 replicate electron pulses. The initial concentration of the contaminant chemicals studied was 100 to 500 μM, far greater than the initial hydroxyl radical concentration of ~3 to 10 μM, and thus ensuring pseudo-first-order kinetic conditions. From the growth kinetics of the transient absorption, it is possible to then obtain the pseudo-first-order rate constant for this reaction and then plot those values against concentration to obtain the overall second-order rate constant (Figure 2.5b).

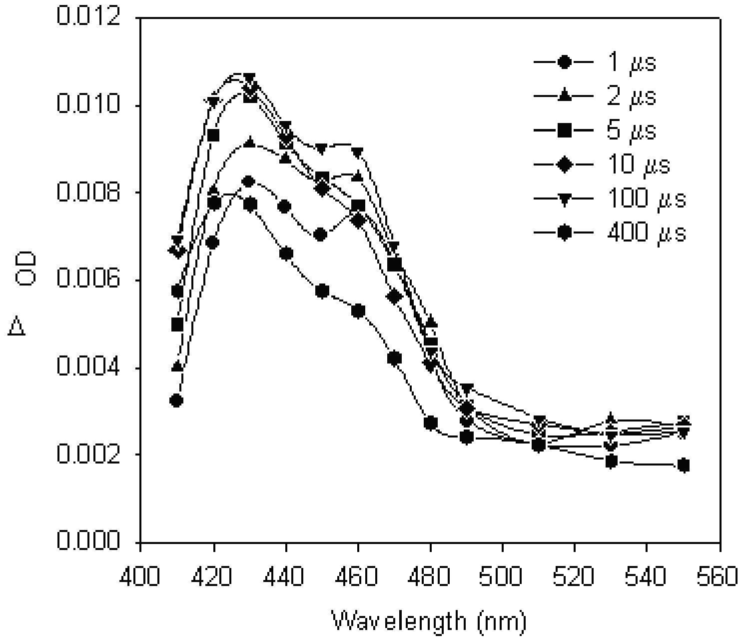


Figure 2.4. Transient spectrum time dependence obtained from hydroxyl radical oxidation of tetracycline.

Table 2.1. Experimental Data Obtained for Tetracycline in This Study

Parameter (units)	**Tetracycline**
$\lambda_{max}^{\bullet OH}$ (nm)	430
$\varepsilon_{max}^{\bullet OH}$ ($M^{-1}cm^{-1}$)	2814
10^9 $k_{\bullet OH}$ ($M^{-1}s^{-1}$)	6.34 ± 0.11 (7.7 ± 1.2)[a]
10^{10} $k_{e_{aq}^-}$ ($M^{-1}s^{-1}$)	2.16 ± 0.08 (1.9)[a]
Initial degradation rate (mM kGy^{-1}) (aerated solution)	0.153 ± 0.008
Initial degradation rate (mM kGy^{-1}) (N_2O-saturated solution)	0.212 ± 0.011
Degradation efficiency of $^{\bullet}OH$ (%)	40 ± 2
Degradation efficiency of e_{aq}^- (%)	23 ± 1

[a] Buxton et al., 1988.

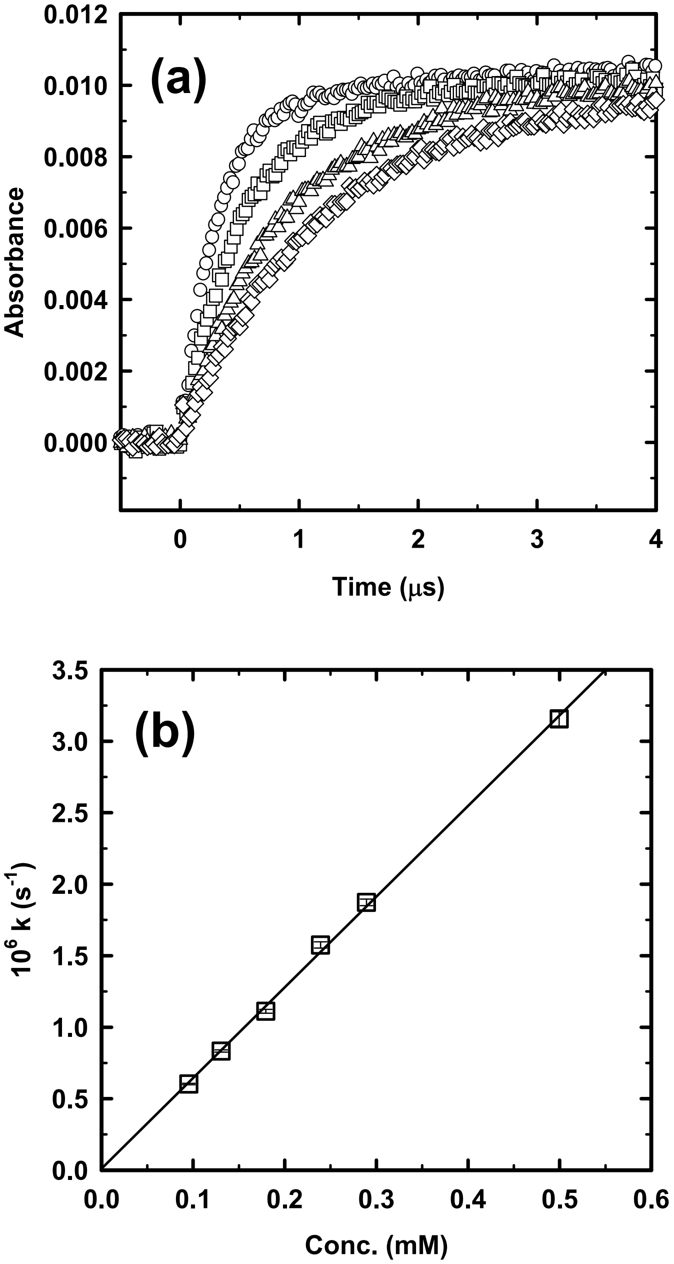


Figure 2.5. (a) Growth kinetics observed at 430 nm for 0.50 (○), 0.29 (□), 0.18 (△), and 0.13 (◇) mM tetracycline in N_2O-saturated water (pH = 7) at room temperature. (b) 2nd-order rate constant determination for hydroxyl radical with tetracycline. Solid line corresponds to weighted linear fit, giving a rate constant of (6.34 ± 0.11) × 10^9 M^{-1} s^{-1}.

2.2.3 Evaluation of $^{\bullet}$OH Reaction Rate Constants using Competition Kinetics

In the case of some compounds, their oxidization reaction with the hydroxyl radical did not yield any significant product radical absorption in the UV-visible region. For these chemicals, it was necessary to use competition kinetics to evaluate $^{\bullet}$OH reaction rate constants. This approach used the thiocyanate ion (SCN^-) in N_2O-saturated solution as a standard. In its reaction with hydroxyl radical, SCN^- forms the transient species $(SCN)_2^{-\bullet}$ ($\varepsilon_{475} = 8100\ M^{-1}\ cm^{-1}$) via the reactions (Spinks and Woods, 1990):

$$^{\bullet}OH + SCN^- \rightarrow {}^-OH + SCN^{\bullet} \qquad [2\text{-}8]$$
$$SCN^- + SCN^{\bullet} = (SCN)_2^{-\bullet} \qquad [2\text{-}9]$$

The rate-limiting step is the first reaction (reaction 2-8), which has a rate constant of $1.1 \times 10^{10}\ M^{-1}\ s^{-1}$ at room temperature (Buxton et al., 1988). In the presence of an $^{\bullet}$OH competitor, for example, chloroacetone (Williams et al., 2002), the $(SCN)_2^{-\bullet}$ absorption is lowered by the fraction of hydroxyl radicals that react with the added substrate (Figure 2.6):

$$^{\bullet}OH + ClCH_2COCH_3 \rightarrow \text{Products} \qquad [2\text{-}10]$$

This $^{\bullet}$OH competition relationship can be solved analytically:

$$\frac{Abs_o(SCN)_2^{-\bullet}}{Abs(SCN)_2^{-\bullet}} = 1 + \frac{k_{2-10}}{k_{2-8}} \times \frac{[ClCH_2COCH_3]}{[SCN^-]} \qquad [2\text{-}11]$$

where $Abs_o(SCN)_2^{-\bullet}$ is the maximum absorption of the thiocyanate radical anion without chloroacetone present and $Abs(SCN)_2^{-\bullet}$ is the measured absorption in the presence of chloroacetone (Figure 2.6).

A plot of the absorption ratio $Abs_o(SCN)_2^{-\bullet}/Abs(SCN)_2^{-\bullet}$ versus the concentration ratio $[ClCH_2COCH_3]/[SCN^-]$ yields a straight line, with an intercept of unity and a slope that corresponds to the rate constant ratio k_{2-10}/k_{2-8} as the slope (Buxton et al., 1988). The k_{2-10} rate constant can then be evaluated from the known k_{2-8} value.

To demonstrate the differences in three related compounds, we show here the second-order rate constant determinations of the hydroxyl radical reaction with chloroacetone, 1,1-dichloroacetone, and 1,1,1- trichloroacetone to be $(1.69 \pm 0.05) \times 10^{8\ 1}$, $(8.9 \pm 0.4) \times 10^7$, and $(3.3 \pm 0.1) \times 10^7\ M^{-1}\ s^{-1}$, respectively (Figure 2.7) by this methodology.

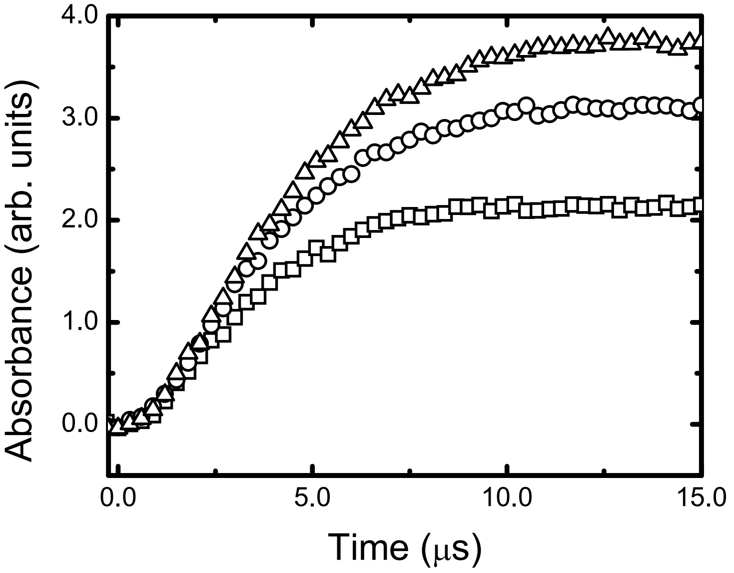


Figure 2.6. Absorption growth at 472 nm of thiocyanate radical dimer, $(SCN)_2^{-\bullet}$, in the absence of chloroacetone (Δ) and with [chloroacetone] = 5.76 × 10^{-4} mol L^{-1} (o) and 1.88 × 10^{-3} mol L^{-1} (□).

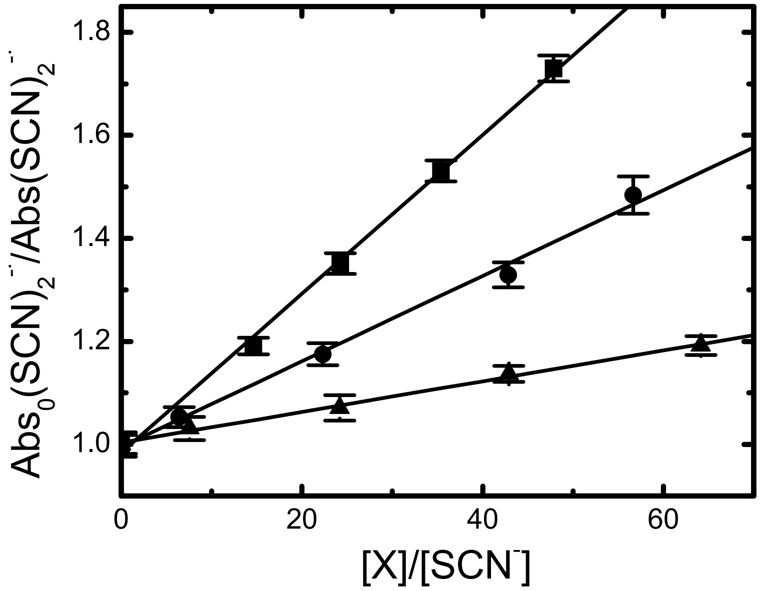


Figure 2.7. 2nd-order rate constant plots for reaction of hydroxyl radical with chloroacetone (□), 1,1-dichloroacetone (o), and 1,1,1-trichloroacetone (Δ). Error bars correspond to 1 standard deviation as derived from nonlinear fitting of the pseudo-1st-order growth curves (Figure 2.4). Straight lines are linear fits corresponding to rate constants of (1.69 ± 0.05) × 10^8, (8.9 ± 0.4) × 10^7, and (3.3 ± 0.1) × 10^7 M^{-1} s^{-1} for chloroacetone, 1,1-dichloroacetone, and 1,1,1-trichloroacetone, respectively.

2.2.4 Evaluation of Hydrated Electron (e^-_{aq}) Reaction Rate Constants

The reactions of the hydrated electron can be directly monitored in real time by observing the rate of change of its extremely strong absorption at 700 nm ($\varepsilon_{700} \sim 21{,}000\ M^{-1}\ cm^{-1}$, see Figure 2.8a). Again from the pseudo-first-order decay kinetics, the second-order reaction rate constant of e_{aq}^- can be determined by plotting the fitted values against the solute concentration (Figure 2.8b).

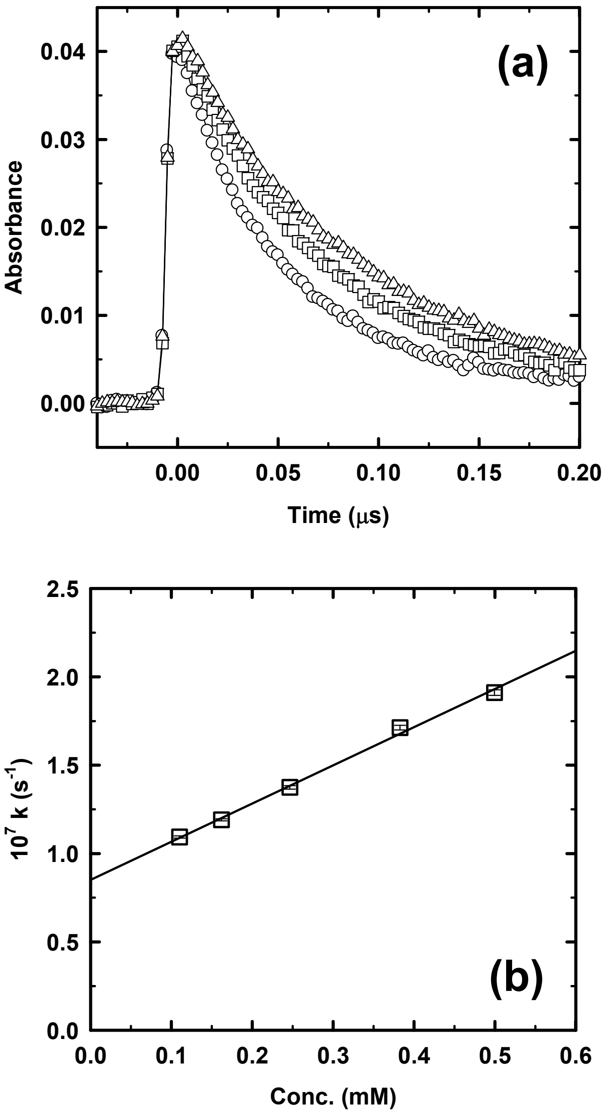


Figure 2.8. (a) Typical kinetic decay profiles obtained for reaction of hydrated electron with tetracycline at 700 nm for 0.50 (○), 0.25 (□), and 0.11 (Δ) mM tetracycline at pH = 7 and room temperature (22 °C). (b) 2nd-order rate constant determination: solid line corresponds to weighted linear fit, giving a rate constant of $(2.16 \pm 0.08) \times 10^{10}\ M^{-1}\ s^{-1}$.

2.3 ^{60}Co AND ^{137}Cs IRRADIATIONS

2.3.1 General Experimental Conditions

The efficiency of the radical reactions and of the radical-induced destruction reaction mechanisms of the model compounds was studied using ^{60}Co gamma radiolysis. Some measurements were also conducted using ^{137}Cs irradiation, which gives exactly the same distribution of water degradation species that ^{60}Co irradiation does. By irradiation of chemical solutions for short periods of time, which corresponds to specific radiation doses, the loss of the model contaminants was quantitatively determined using chromatography methods, namely, HPLC, gas chromatography/mass spectometry (GC/MS), or liquid chromatography/mass spectometry (LC/MS). Moreover, the loss of the parent compounds could also be correlated with the appearance of radical-induced-destruction by-products. The latter were also identified and quantified by using standard LC/MS analytical techniques.

The ^{60}Co sources at the Radiation Laboratory on the University of Notre Dame campus are shown in Figure 2.9. The ^{60}Co isotope is a gamma emitter and creates the conditions exemplified in Equation 2-2 for the radiolysis of water.

Figure 2.9. ^{60}Co sources housed at Notre Dame Radiation Laboratory.

The experimental details described in Section 2.1 apply to the steady-state gamma radiolysis experiments in addition to the electron pulse radiolysis. Both oxidizing and reducing conditions can be established, as well as aerated or nonaerated conditions, by simply adjusting the chemical conditions.

2.3.2 Determination of Radical Reaction Efficiencies

The following description is an example of how individual degradation efficiencies for hydroxyl radical and hydrated electron reactions were determined in this study (Song et al., 2008a). In this specific case we have again used tetracycline as the example, starting with a high initial solute concentration of 0.5 mM. This tetracycline concentration was deliberately chosen to ensure that radical reactions with secondary by-products were negligible, especially at short irradiation times. This provision allowed us to isolate only the tetracycline oxidation chemistry.

Of the three radicals produced in the water irradiation, only the hydroxyl radical and hydrated electron reactions need to be considered. (The hydrogen atom was not considered in this portion of the study, because of its low initial yield and high reactivity with any dissolved oxygen present.) The specific reaction rate constant, for each of the two radicals considered with tetracycline, was determined as described in sections 2.2.3 and 2.2.4.

Equation 2-2 describes the radiolysis of water and gives the quantitative yields for each species produced during the gamma irradiation. The loss of tetracycline (TC in the equations below) concentration through the induced radical reactions can be directly measured under different redox conditions and through manipulation of the chemical conditions, as shown in Figure 2.10. The initial loss rates (initial slopes) can be evaluated from these data, as again shown in Figure 2.10. These slopes are described by the sum of the two individual radical-induced degradation reactions, caused by the reaction of each species multiplied by its own individual degradation efficiencies:

$$\text{Initial slope} = E_{^\bullet OH} \times Y_{^\bullet OH} + E_{e^-_{aq}} \times Y_{e^-_{aq}} \qquad [2\text{-}12]$$

In this equation the $Y_{^\bullet OH}$ and $Y_{e^-_{aq}}$ values are the initial radical yields for each species (Equation 2-2) and the $E_{^\bullet OH}$ and $E_{e^-_{aq}}$ numbers are the corresponding degradation efficiencies. The specific yields of each radical are dependent upon the irradiation conditions but can be calculated using known rate constants. For example, under aerated conditions, all of the hydroxyl radicals produced react with tetracycline, giving a $Y_{^\bullet OH}$ value of 0.28 μmol J^{-1}. However, the e^-_{aq} reaction will be partitioned between the tetracycline and dissolved oxygen as follows:

$$e^-_{aq} + TC \rightarrow \text{products} \qquad k_{TC} \qquad [2\text{-}13]$$

$$e^-_{aq} + O_2 \rightarrow {}^\bullet O_2^- \qquad k_{O_2} = 1.9 \times 10^{10}\ M^{-1}\,s^{-1} \qquad [2\text{-}14]$$

Assuming that the reaction of superoxide radical (${}^\bullet O_2^-$) with tetracycline is negligible, the $Y_{e^-_{aq}}$ that reacts with TC can be calculated by the following equation:

$$Y_{e^-_{aq}} = 0.27 \times \frac{k_C[TC]}{k_C[TC] + k_{O_2}[O_2]_{aq}} \qquad [2\text{-}15]$$

If one uses the tetracycline reduction rate constant ($k_{TC} = 2.16 \times 10^{10}\ M^{-1}s^{-1}$), the initial tetracycline concentration (5.0×10^{-4} M), and the concentration of dissolved oxygen ($[O_2]_{aq} = 2.5 \times 10^{-4}$ M), the calculated value for $Y_{e^-_{aq}}$ is 0.190.

Under oxidizing N_2O-saturated conditions, the reaction of e^-_{aq} is partitioned by the competition reaction of N_2O instead of dissolved oxygen, as follows:

$$e^-_{aq} + TC \rightarrow \text{products} \qquad k_C \qquad [2\text{-}16]$$

$$e^-_{aq} + N_2O + H_2O \rightarrow {}^\bullet OH + OH^- + N_2 \qquad k_{N_2O} = 9.1 \times 10^9\ M^{-1}\ s^{-1} \qquad [2\text{-}17]$$

If one uses the aqueous saturated concentration of N_2O (2.41×10^{-2} M) at our solution temperature, the value for $Y_{e^-_{aq}}$ is calculated as shown in Equation 2-15. For tetracycline, the calculated value for e_{aq}^- is 0.013. In this condition, because e^-_{aq} is converted to ${}^\bullet OH$ by the reaction with N_2O, the value of $Y_{{}^\bullet OH}$ is higher than 0.28, being the sum of all pathways that generate this radical, and can be calculated as follows:

$$Y_{{}^\bullet OH} = 0.28 + 0.27 \times \frac{k_{N_2O}[N_2O]}{k_{TC}[TC] + k_{N_2O}[N_2O]} \qquad [2\text{-}18]$$

From this equation, the total value of $Y_{{}^\bullet OH}$ under these conditions is 0.537.

Assuming that the efficiency values, $E_{{}^\bullet OH}$ and $E_{e^-_{aq}}$, are not affected by the experimental conditions, they can be determined from two initial slopes measured under N_2O-saturated and aerated conditions. Using the measured initial slopes, we have

$$0.153 \pm 0.008 = 0.28 \times E_{{}^\bullet OH} + 0.191 \times E_{e^-_{aq}} \qquad [2\text{-}19]$$

$$0.212 \pm 0.011 = 0.537 \times E_{{}^\bullet OH} + 0.013 \times E_{e^-_{aq}} \qquad [2\text{-}20]$$

These equations give $E_{{}^\bullet OH} = 0.389 \pm 0.007$ and $E_{e^-_{aq}} = 0.228 \pm 0.011$. By considering all errors involved in this analysis and converting to percentages, we obtain reaction efficiencies for the OH radical and hydrated electron to be 40 ± 2 and 23 ± 1%, respectively. This finding implies that for all the hydroxyl radicals that react with tetracycline in aqueous solution, only 40% of these reactions will result in a different product species (destruction of the parent contaminant as defined by being differentiable in an HPLC analysis). This finding is similar for the hydrated electron reaction.

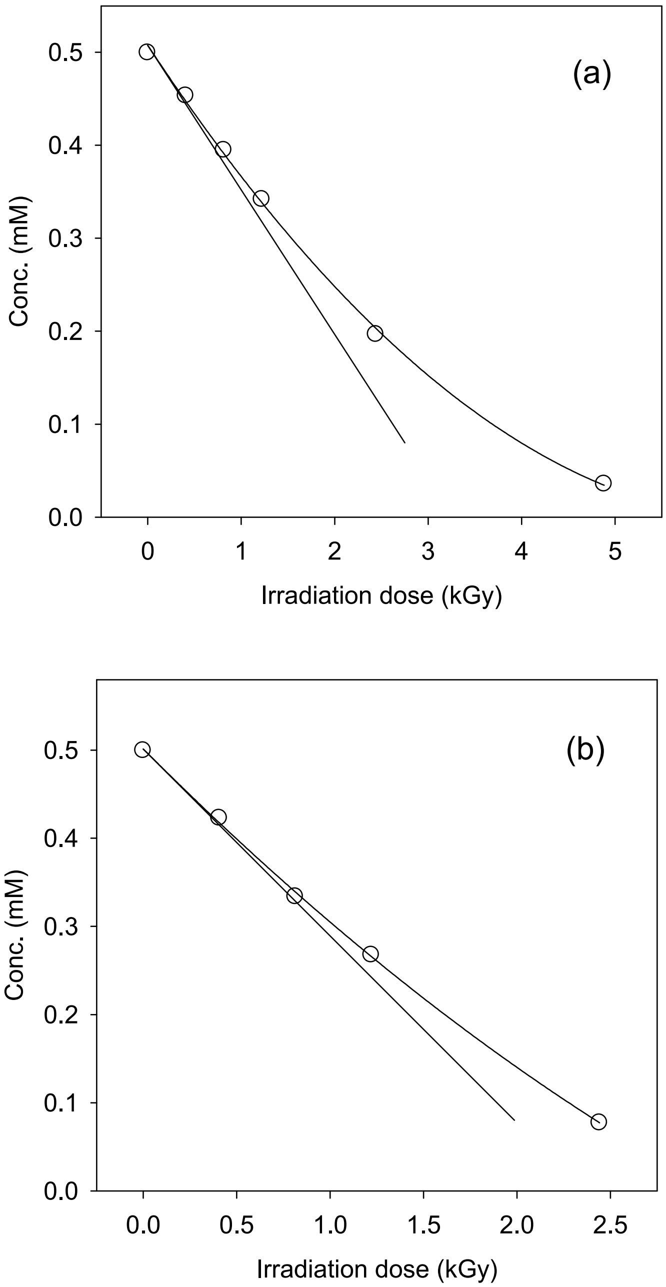


Figure 2.10. Degradation of tetracycline by ^{60}Co irradiation in (a) aerated and (b) N_2O-saturated aqueous solution. Curves are the fitted quadratic function, and straight lines correspond to initial slopes with values of 0.153 ± 0.007 mM kGy^{-1} and 0.212 ± 0.011 mM kGy^{-1}, respectively.

CHAPTER 3

RATE CONSTANTS AND REACTION MECHANISMS

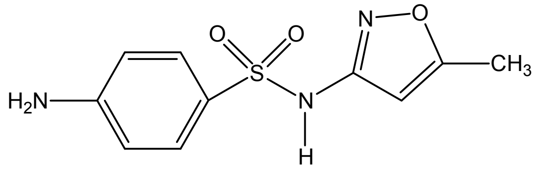
The goal of our project research was to provide the kinetic, efficiency, and mechanistic data necessary to develop computer models that accurately described the underlying chemistry for microcontaminant removal from real-world waters using AOPs. This work required measuring absolute reaction rate constants for selected classes of wastewater contaminants by using both oxidizing hydroxyl radical (•OH) and reducing hydrated electron (e^-_{aq}) reactions, elucidating the individual radicals' reaction efficiencies, and determining the ultimate stable products produced in these reactions. While the rate constant data were more easily obtained in high-quality waters and these results were directly transferable to real-world waters, both the radicals' efficiency and ultimate stable product studies had to be conducted in multiple water qualities, as the real water components (dissolved organic matter [DOM], carbonate, etc.) significantly impacted these parameters.

Many microcontaminant classes are important. We chose to focus on a number of pharmaceuticals known to occur in water. However, we also studied several other compounds, such as the common insect repellent *N,N*-diethyl-*meta*-toluamide (DEET); the harmful algal toxins domoic and kainic acids; and mycrocystin-LR, BPA, and a number of dissolved organic isolates from natural waters and wastewater effluents (see Table E.1). The compound bimolecular reaction rate constants are summarized in Table E.1 in the Executive Summary and are also listed below.

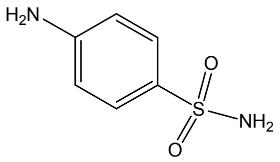
3.1 SULFA DRUG ANTIBIOTICS

Sulfa drugs represent a class of chemical compounds used for a variety of antibiotic needs, including: treatment of human infections, veterinary medicine, aquaculture, and even some herbicide applications. Their presence in aquatic ecosystems has been documented, creating a need to understand the effectiveness of advanced oxidation and/or reduction chemistry (Hirsch et al., 1999; Khetan and Collins, 2007).

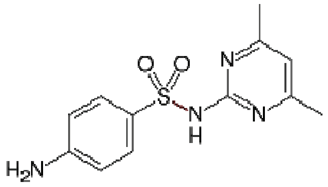
The absolute kinetics and efficiencies of the hydroxyl radical and hydrated electron with a selected group of sulfonamides (sulfa drugs) were determined (Mezyk et al., 2007). The four major sulfonamides investigated were sulfamethazine, sulfamethizole, sulfamethoxazole, and sulfamerazine, all of which contain the main structural sulfa drug component, sulfanilamide. The structures of the four sulfa drugs and sulfanilamide are as follows:



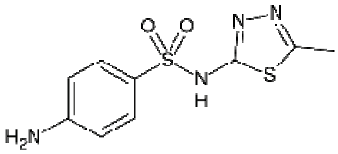
sulfamethoxazole



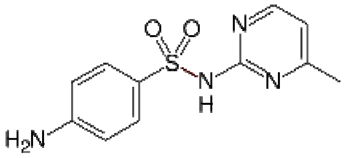
sulfanilamide



sulfamethazine



sulfamethizole



sulfamerazine

Figure 3.1. Chemical structures for the 5 sulfa drugs studied during this project.

Rate constants were determined for the reaction of the hydroxyl radical with each sulfa drug and with sulfanilamide, following the methods detailed previously, and the consistency of these values suggests a common reaction mechanism at the benzene ring (see Table 3.1). This finding is in agreement with multiple steady-state product analyses that we conducted using HPLC techniques, where the irradiated solutions were void of sulfanilic acid, a breakdown product identified in the hydrated electron reactions.

Table 3.1. Summary of Hydroxyl Radical and Hydrated Electron Reaction Rate Constants with Sulfonamides[a]

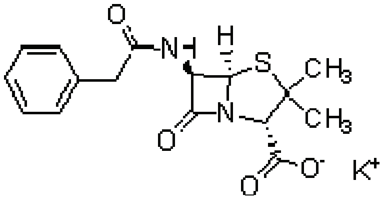
Compounds	Reaction Rate $^{\bullet}$OH (M^{-1} s^{-1})	Reaction Rate e^-_{aq} (M^{-1} s^{-1})
Sulfamethazine	$(8.3 \pm 0.8) \times 10^9$	$(2.4 \pm 0.1) \times 10^{10}$
Sulfamethizole	$(7.9 \pm 0.4) \times 10^9$	$(2.0 \pm 0.1) \times 10^{10}$
Sulfamethoxazole	$(8.5 \pm 0.3) \times 10^9$	$(1.0 \pm 0.03) \times 10^{10}$
Sulfamerazine	$(7.8 \pm 0.3) \times 10^9$	$(2.0 \pm 0.05) \times 10^{10}$
Sulfanilamide[b]	1.6×10^9	

[a] Mezyk et al., 2007.

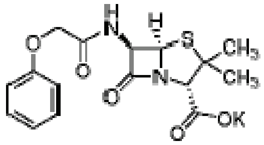
[b] Phillips et al., 1973.

3.2 ß-LACTAM ANTIBIOTICS

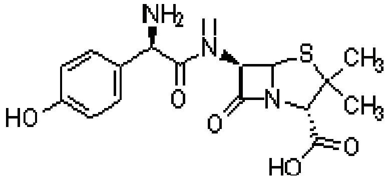
ß-Lactam antibiotics are also utilized in massive quantities in the United States and Europe. Their presence in natural waters has been well substantiated (Hirsch et al., 1999) and their removal in conventional wastewater treatment plants summarized (Paxeus, 2004). For this study, several ß-lactams were selected: penicillin G, penicillin V, and amoxicillin. The model compound (+)-6-aminopenicillanic acid was also studied:



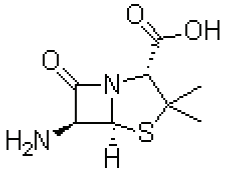
Penicillin G



Penicillin V



Amoxicillin



(+)-6-Aminopenicillanic acid

Figure 3.2. Chemical structures of the 3 antibiotics and a model compound studied.

Rate constants for each of these compounds with the hydroxyl radical and with the hydrated electron were determined (Song et al., 2008a) and are shown below in Table 3.2.

Table 3.2. Summary of Hydroxyl Radical and Hydrated Electron Reaction Rate Constants with β-Lactams

Compound	Reaction Rates $^{\bullet}OH$ (M^{-1} s^{-1})	Reaction Rates e^{-}_{aq} (M^{-1} s^{-1})
Penicillin G	$(7.97 \pm 0.11) \times 10^9$	$(3.92 \pm 0.10) \times 10^9$
Penicillin V	$(8.76 \pm 0.28) \times 10^9$	$(5.76 \pm 0.24) \times 10^9$
Amoxicillin	$(6.94 \pm 0.44) \times 10^9$	$(3.47 \pm 0.07) \times 10^9$
(+)-6-Amino-penicillanic acid	$(2.40 \pm 0.05) \times 10^9$	$(3.35 \pm 0.06) \times 10^9$

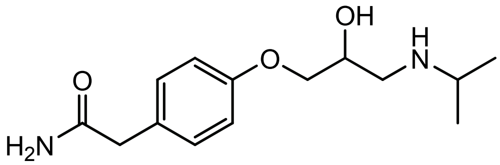
Within the structures of penicillin G, penicillin V, and amoxicillin is the benzene ring, the common moiety that is favored for reaction of the electrophilic hydroxyl radical. The high rate constants for these three β-lactams with the hydroxyl radical reflect this favored chemical pathway (6.9 to 8.8 × 10^9 M^{-1} s^{-1}). The model compound (+)-6-aminopenicillanic acid does not contain this structural moiety and consequently shows a significantly lower rate constant, 2.40 × 10^9 M^{-1} s^{-1}.

The reaction rate constants of these four compounds with the hydrated electron were very similar. In comparison to the rate constant for benzene reduction in water (~1.0 × 10^7 M^{-1} s^{-1}), the hydrated electron reactions with these β-lactams are far faster, indicating that the reduction takes place at the common β-lactam structural portion (amide function bonded to the four- and five-membered fused rings) of the molecules.

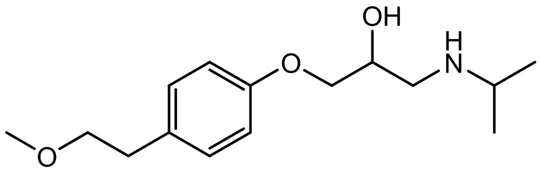
In summary, for the antibiotics studied, both the β-lactams and sulfonamides react quickly with oxidizing hydroxyl radicals and reducing hydrated electrons, suggesting that they would both be effectively destroyed by using radicals formed in AO/RPs. However, it is clear that the reactivity of the radicals depends on the specific antibiotic structure.

3.3 ß-BLOCKERS

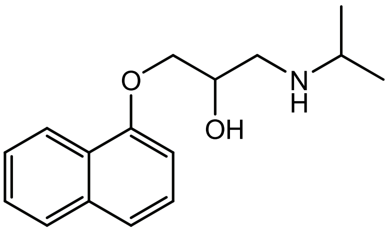
Atenolol and metoprolol are two common ß-blockers, compounds used to treat cardiovascular disorders such as hypertension and arrhythmias. These medicinal compounds have been available for quite a long time in both the United States and in Europe, and typical wastewater treatment plants remove only a small percentage of them (Paxeus, 2004). While a few earlier studies have shown the effective nature of the hydroxyl radical in the breakdown of these drugs, only limited by-product data and kinetic information have been previously reported (Andreozzi et al., 2003; Ternes et al., 2002).



atenolol



metoprolol



propranolol

Figure 3.3. Chemical structures of β-blockers in this study.

In this work, absolute reaction rate constants were determined for atenolol, metoprolol, and propranolol (Figure 3.3), and gamma irradiation experiments were performed on aerated solutions of each ß-blocker for product analysis studies using LC/MS (Song et al., 2008b). Similarly to the previously reported compounds, the three ß-blockers have a benzene ring-based structure that offers the hydroxyl radical an electron-rich site for reactions. This mechanistic hypothesis is consistent with the measured hydroxyl radical rate constants as shown in Table 3.3.

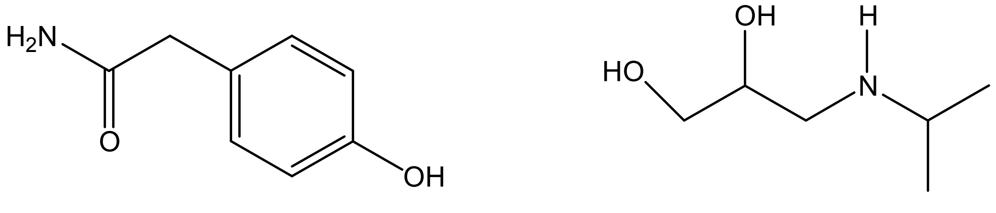
Table 3.3. Summary of Hydroxyl Radical and Hydrated Electron Reaction Rate Constants with β-Blockers in Aqueous Solution[a]

Compound	Reaction Rate $^{\bullet}OH$ (M^{-1} s^{-1})	Reaction Rate e^{-}_{aq} (M^{-1} s^{-1})
Atenolol	$(7.05 \pm 0.27) \times 10^{9}$	$(5.91 \pm 0.21) \times 10^{8}$
Metoprolol	$(8.39 \pm 0.06) \times 10^{9}$	$(1.73 \pm 0.03) \times 10^{8}$
Propranolol	$(1.07 \pm 0.02) \times 10^{10}$	$(1.26 \pm 0.02) \times 10^{10}$

[a] Song et al., 2008b.

In contrast, the hydrated electron rate constants varied over 2 orders of magnitude, suggesting different reductive reaction sites in these three molecules. However, while both types of radicals (oxidizing hydroxyl radicals and reductive hydrated electrons) are created in aerated aqueous solutions subjected to ionizing radiation, the hydrated electrons predominantly react with the dissolved oxygen to form the inert superoxide anion ($O_2^{-\bullet}$), and therefore conditions for oxidative radical reactions dominate. This lack of reduction will be further enhanced by the relatively low hydrated electron reaction rate constants measured for atenolol and metoprolol.

Product analyses of the irradiated, aqueous atenolol, propranolol, and metoprolol solutions showed similar hydroxyl radical reactivity, initiated by the reaction of this radical with the aromatic ring. With atenolol (molecular weight [MW] = 266), propanolol (MW = 259), and metoprolol (MW = 267), dominant oxidation products were the corresponding hydroxylated forms (MW = 282, 275, and 283, respectively), and the compounds formed from the ipso attack/loss of the ether group, both of which were observed for atenolol oxidation.



MW = 151

MW = 133

Figure 3.4. Tentative structures of reaction by-products of atenolol.

The common ether side chain on the three ß-blockers cleaves from the aromatic rings in the oxidation reactions to form the ß-amino diol shown above with a molecular mass of 133. While this molecule was readily detected for all three of the irradiated ß-blockers, it reached a maximum concentration at approximately 7 kGy and then decreased again in concentration. Consequently, this oxidation product does not persist and, like the other identified products of the hydroxyl radical reactions, is readily affected by further generated $^\bullet$OH. After a radiation dose of about 3 kGy, the concentration of the β-blockers decreased to less than 50% of the original 1.0 mM, further proving the ability of the hydroxyl radical to effectively remediate these prevalent pharmaceuticals in water solutions.

3.4 BPA

BPA [2,2-*bis*-(4-hydroxyphenyl)propane] has recently been the center of controversy in the world of plastics because of its suspected endocrine-disrupting potential (Bannister et al., 2007). The main pathway for natural water contamination of BPA is from industrial wastewaters mixed with sewage wastewaters (Furhacker et al., 2000) and not from the leaching of the polycarbonate plastic material for which it is a key starting material.

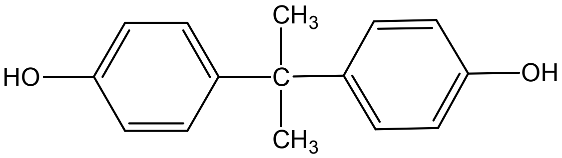


Figure 3.5. Chemical structure of BPA.

BPA has two electron-rich aromatic rings and was determined from electron pulse experiments to react quite rapidly with the hydroxyl radical, having a rate constant of $6.9 \pm 0.2 \times 10^9\ M^{-1}\ s^{-1}$ (Peller et al., 2009). The hydroxyl radical reacts with one of the benzene rings and forms the hydroxylated form of the compound, as expected and as verified by LC/MS analysis. This oxidation product was readily detected in the HPLC data when clean deionized water solutions were irradiated.

Since real water environments are far from clean, unlike deionized water solutions, further experiments were conducted using various treated and characterized wastewaters. BPA was dissolved in secondary-treated wastewater (before membrane filtration), and electron pulse radiolysis experiments were performed on these samples by using nitrous oxide saturated solutions. (Note: only oxidizing hydroxyl radical reactions occurred.) Results revealed the same initial hydroxyl radical reaction on the aromatic ring but subsequent chemical pathways in the treated wastewater different from that noted in the higher-purity laboratory water. Steady-state experiments verified the alternate chemical pathway(s) for the hydroxyl radical oxidation of BPA, namely, by the absence of the hydroxylated form of BPA in the HPLC data. Even though a different chemical pathway is taken by the hydroxyl radical in the wastewater medium, BPA is still oxidatively destroyed. A complete study of the efficiency of the hydroxyl radical with BPA in various water media is reported in Chapter 4.

3.5 DEET

The common insect repellent DEET is used around the world in massive quantities and, to no surprise, is detected in many bodies of water. An extensive 2002 study reported the presence of up to 0.50 µg of DEET/L in 25% of U.S. streams and water samples and levels as high as 0.066 µg/L in treated wastewater samples (Kolpin et al., 2002). Another study indicated that levels of DEET were as high as 1.1 µg/L in 74% of water samples from 54 U.S. streams (Vanderford et al., 2003).

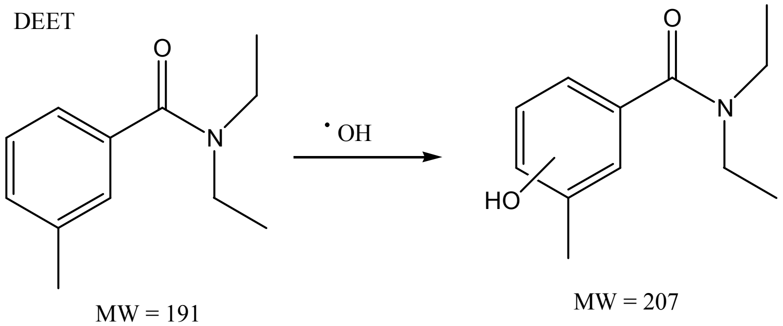


Figure 3.6. Chemical structure of DEET and 1st reaction by-product from hydroxyl radical attack.

The relatively simple structure of DEET consists of the methylbenzene moiety and a diethylamide functionality. Once again, the hydroxyl radical chemistry is predicted to occur mainly at the benzene ring, and LC/MS analysis verified formation of the hydroxylated product (MW = 207) (Song et al., 2009a). The bimolecular rate constant for this reaction was determined to be $(4.95 \pm 0.18) \times 10^9\ M^{-1}\ s^{-1}$ in agreement with the value reported by Zhang and Lemley using competition kinetics (2006). The rate constant for the reaction of DEET with the hydrated electron in this study was directly determined as $(1.34 \pm 0.04) \times 10^9\ M^{-1}\ s^{-1}$.

Gamma radiolysis experiments were also performed with aerated solutions of DEET for the determination of reaction efficiencies and degradation products. These radical reactions with DEET were determined to be nearly 100% efficient for both radicals. Several decomposition products were identified, and reaction pathways were proposed (Song et al., 2009a). The main reaction mechanism is the hydroxyl radical addition, which is often followed by a second $^{\bullet}OH$ addition to the ring and is expected, since the dihydroxylated product was observed (MW = 223). Minor pathways appear to involve peroxyl intermediates (because of the presence of oxygen in the solutions) that lead to small amounts of both oxidized and reduced degradation products.

3.6 MICROCYCSTIN-LR

Cyanobacteria (blue-green algae) produce toxic compounds termed cyanotoxins. Of interest in water treatment and water reuse is that these organisms are freshwater species, as opposed to many harmful algal bloom toxins that arise from marine organisms, which would not likely be found in any appreciable concentration in reused waters. The most common type of cyanotoxins present in potable water is the group of cyclic heptapeptides known as microcystins. The following example is of the macrostructural cyclic heptapeptide, microcystin-LR (Figure 3.7).

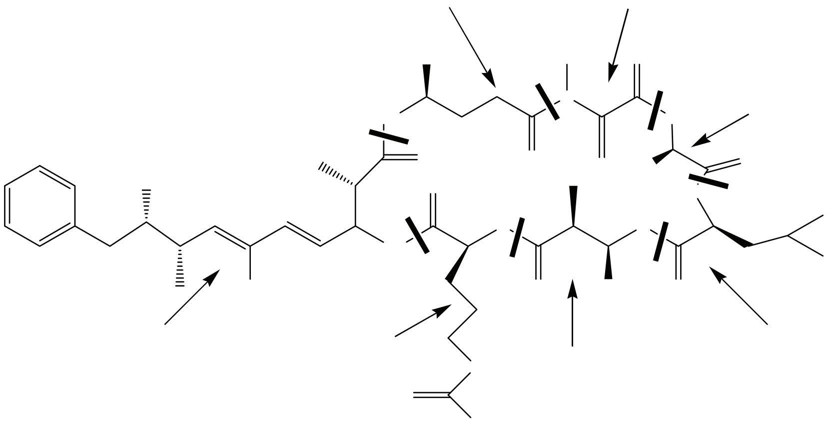


Figure 3.7. Chemical structure of mycrocystin-LR. Note: there are two main structural entities that make up the molecule: (1) the side chain with two double bonds and a terminal benzene moiety, and (2) a cyclic protein portion of the molecule.)

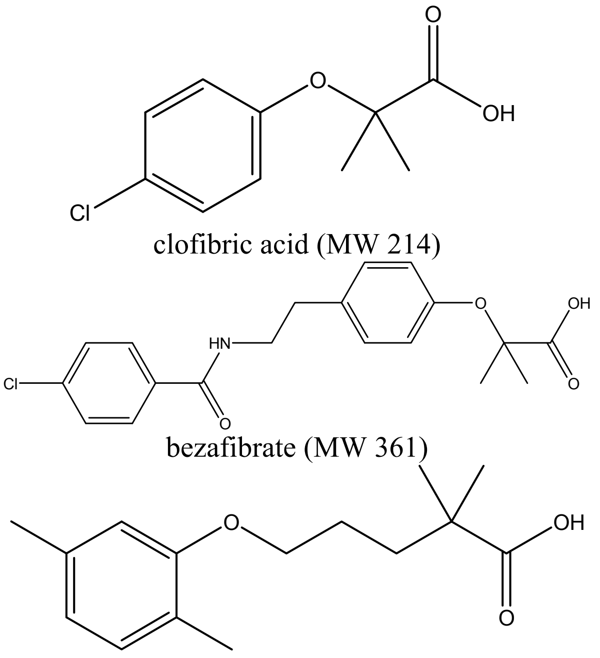
This work was undertaken to better evaluate the reaction rate constant of microcystin-LR with the hydroxyl radical. The absolute reaction rate constant as determined by competition kinetics was $(2.3 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1}. Overall, it is clear that the hydroxyl radical reacts at several different sites on the molecule, and by analyzing the data it was possible to apportion the reactivity of the molecule. The benzyl moiety accounted for $(1.03 \pm 0.03) \times 10^{10}$ M^{-1} s^{-1}, while the sum of the individual rate constants for the peptide portion of the molecule was 2.1×10^{10} M^{-1} s^{-1}.

While the benzene ring is the most obvious site for hydroxyl radical reactivity, hydrogen atom abstraction reactions, which are slower by 1 or 2 orders of magnitude, may also play a factor in the degradation. The mycrocystin-LR molecule offers more than 50 sites for H-atom abstraction, and the competition kinetics rate value being twice as high as the $^{\bullet}OH$ transient spectral value points to a variety of reactions making up the hydroxyl radical chemistry.

Radical-induced degradation products were identified from the gamma-irradiated solutions of LR-microcystin, and mechanisms were proposed for the initial hydroxyl radical transformations (Song et al., 2009b). The product studies indicate that the ADDA portion (3-amino-9-methoxy-2,6,8-trimethyl-10-phenyl-4,6-dienoic acid) of the molecule is the major reaction site initially and that destruction of this site leads to loss of biological activity. This structural entity is also present in microcystin variants (>80%), allowing for the prediction of successful hydroxyl radical reactivity with other similar molecules.

3.7 FIBRATE PHARMACEUTICALS

Fibrate pharmaceutical compounds belong to the class of phenoxyalkanoic acids and function as blood lipid regulators. Because of the persistence of clofibric acid in the environment and the extensive use of these compounds, three closely related compounds that are used to lower blood cholesterol levels were studied. The structure of these compounds follows:



clofibric acid (MW 214)

bezafibrate (MW 361)

gemfibrozil (MW 250)

Figure 3.8. Chemical structures of 3 fibrate compounds studied.

Absolute bimolecular rate constants were determined for the hydroxyl radical and hydrated electron for these three compounds and are shown in Table 3.4 below (Razavi et al., 2009). All three compounds react rapidly with the hydroxyl radical via $^{\bullet}$OH addition to the aromatic ring but show more variation in the hydrated electron reaction.

Table 3.4. Summary of Hydroxyl Radical and Hydrated Electron Reaction Rate Constants with Fibrate Pharmaceuticals[a]

Compound	Reaction Rates (M^{-1} s^{-1})	
	$^{\bullet}$OH	e^{-}_{aq}
Clofibric Acid	$(6.98 \pm 0.12) \times 10^{9}$	$(6.59 \pm 0.43) \times 10^{8}$
Bezafibrate	$(8.00 \pm 0.22) \times 10^{9}$	$(1.12 \pm 0.03) \times 10^{10}$
Gemfibrozil	$(10.0 \pm 0.60) \times 10^{9}$	$(6.26 \pm 0.58) \times 10^{8}$

[a] Razavi et al., 2009.

Steady-state experiments on these compounds were conducted using a ^{137}Cs source. The dose rates varied from 4.2×10^3 Gy h^{-1} to less than 5×10^2 Gy h^{-1}. Extensive product analyses were done on the gamma-irradiated compound solutions that were subjected to hydroxyl radical-mediated degradation conditions. In the case of clofibric acid, the initial hydroxyl radical reaction can occur via different possibilities: substitution of the Cl moiety, substitution of the ether group, or addition of the $^{\bullet}$OH radical to the ring. All of these possible pathways result in compounds that were identified in the MS analyses. Benzafibrate possesses two different aromatic moieties, and the hydroxyl radical reactions resulted in 10 separable early oxidation products. Irradiation of gemfibrozil led to the formation of mono-, di-, and trihydroxylated products, according to the MW analyses of the oxidative degradation products. Relative concentrations of all the degradation products were quantitatively assessed and indicated that the products of the clofibric acid showed the greatest potential for real-world water persistence.

One of the principal shortcomings of all of the studies conducted with the pharmaceutically active compounds was that there was no way to determine the biological activity of the by-products. We believe that this aspect deserves considerable further study.

3.8 DOM

DOM, whether it is obtained from a wastewater treatment plant or from natural sources such as a river, constitutes one of the most significant hydroxyl radical scavengers in AOP-based water treatment. Our study here provided the first report of the absolute bimolecular reaction rates for isolated DOM fractions (Westerhoff et al., 2007). Seven DOM isolates from three different sources were fractionated by column chromatography with different resins, which resulted in samples that differed in UV absorbance at 254 nm and C/N ratio. Reaction rates with the DOM samples were determined by both competition kinetics and direct transient absorption measurements. These results are summarized in Table 3.5.

Table 3.5. Summary of Hydroxyl Radical Reaction Rate Constants with DOM Fractions[a]

DOM description	$^{\bullet}$OH (M^{-1} s^{-1})
Suwannee River fulvic acid[b]	$(1.39 \pm 0.16) \times 10^8$
Suwannee River fulvic acid[b]	$(1.87 \pm 0.07) \times 10^8$
Suwannee River fulvic acid[b]	$(1.55 \pm 0.04) \times 10^8$
Saguaro Lake hydrophobic acid	$(1.73 \pm 0.04) \times 10^8$
Saguaro Lake hydrophilic acid	$(1.45 \pm 0.02) \times 10^8$
Saguaro Lake hydrophobic neutral	$(2.18 \pm 0.13) \times 10^8$
Nogales WWTP hydrophobic neutral	$(1.72 \pm 0.13) \times 10^8$
Nogales WWTP transphilic neutral	$(4.53 \pm 0.54) \times 10^8$
Nogales WWTP transphilic acid	$(3.63 \pm 0.31) \times 10^8$

[a] Westerhoff et al., 2007.

[b] Multiple rate constant determinations of same Suwannee River fulvic acid sample using either direct or SCN$^-$ competition kinetics method.

An interesting observation in these DOM pulse radiolysis experiments was the stability of the $DOM^{\bullet}$ transient absorptions, which remained intact even above the millisecond timescale. This observation implies some additional stability of this oxidized radical is occurring; possible reasons include the presence of molecules that can be electron shuttles, such as quinones and semiquinones. The reaction rates reported above suggest that in many treatment plants it will be necessary to reduce the organic content of the water if AOPs are to be considered.

These data instigated several additional investigations further analyzing several aspects of DOM using radiation techniques. This portion of our study was inspired by the data reported by Westerhoff et al. (2007) (summarized above) and is the first in a series of papers exploring the application of the techniques of radiation chemistry to better understand the structure, reactivity, and chemistry of DOM. The goal of these studies is to better understand the structure and reactivity of natural DOM in aquatic environments. A more detailed knowledge of these DOM characteristics would lead to a better understanding of carbon cycling in natural waters and processes associated with water treatment using free-radical chemistry. Our specific interest in DOM in natural waters is severalfold: (1) the photochemical formation of reactive oxygen species, (2) photobleaching of the DOM in coastal oceans, (3) the use of chromophoric DOM as a tracer of water masses and in carbon cycling, and (4) and a better understanding of implications in water reuse treatment processes. The first paper in this series reports on some additional representative organic compounds, the oxidized transients they form, and their comparison to DOM transients (Cooper et al., 2008).

CHAPTER 4

HYDROXYL RADICAL-MEDIATED OXIDATION OF SELECTED PROBLEMATIC ORGANIC CONTAMINANTS IN TREATED WASTEWATERS

4.1 BACKGROUND

The development of an innovative method for quantitatively evaluating the radical-induced degradation of water contaminants by AOPs, using gamma radiolysis of chemicals in real-world water matrices, was initiated in the early stages of this project. The treatment of wastewaters containing low levels of organic contaminants is extremely challenging, and trying to understand the effects of other dissolved substances further complicates the challenge. While utilization of AOP techniques that form the hydroxyl radical is a large-scale option being considered by utilities, many chemical details of these technologies are unexplored. The efficiency of AOPs depends, to a large extent, on the water quality, and this connection became the emphasis of this part of the project.

As a starting point for this portion of the project, samples of wastewaters of different quality were spiked with the chemical contaminant BPA (or another organic contaminant) and sparged with $N_2O(g)$ to promote only hydroxyl radical-mediated oxidation processes (see Chapter 2). The spiked solutions were irradiated with a ^{60}Co source (gamma emitter) for different lengths of time that corresponded to different radiation doses, and the removal of the organic compound was measured using HPLC techniques.

After several preliminary experiments, it became clear that to obtain quantitative data on the hydroxyl radical reactions for engineering applications, degradation removal values that were not dependent upon the initial concentrations of contaminants had to be determined. Based on multiple experimental observations, the following early conclusions were made:

(1) Measured removal efficiencies are significantly influenced by the further radical reactions with the radical-induced products (stable compounds produced from the original reactions), especially when the rate constants for these latter reactions are much higher than the reaction with the initial solute. To obtain quantitative radical-induced removal data for only single contaminants, *high* initial solute concentrations with respect to the number of generated hydroxyl radicals have to be used, even if this situation does not correspond to real-world conditions.

(2) As product interference is compounded at larger doses, only the *initial slopes* should be used for quantitative evaluations and comparisons. The larger the delivered dose, the more hydroxyl radicals are generated and the more parent compound degradation occurs. In order to assess the ability of the hydroxyl radical to oxidize the organic contaminant of interest, it is important to effect a change in only about 10 to 20% of the initial contaminant concentration. Therefore, we were careful to choose the correct contaminant concentration and dose for our gamma radiolysis experiments.

We then redefined dose constants as ***removal constants*** for the hydroxyl radical-mediated degradations of the contaminants. The ***removal constants*** are calculated by computing the slope of the curve obtained from the graph of the absolute change in concentration of the contaminant against absorbed radiation dose. Then the ***efficiency*** (the percentage of hydroxyl radicals that oxidatively degrade the contaminant) of the reaction of the compound with the hydroxyl radical under the specified conditions can be properly determined. For accurate quantification of the hydroxyl radical oxidation of the model contaminants, the early stages of the degradation must be followed. Preliminary results with BPA substantiated this requirement of early-stage analysis, since the slope of the reaction curve changes substantially after the first 20% degradation.

4.2 INFLUENTIAL DISSOLVED SPECIES

Wastewaters of different quality were supplied, mainly from Orange County, California, and to a lesser extent from Scottsdale, Arizona's water treatment facility. For both cases, a full characterization of the water accompanied the supply of water and revealed the main dissolved species typical of treated wastewater. Early experiments showed effects from bicarbonate and DOM (or total organic carbon [TOC]), whereas experiments with nitrates and sulfates and phosphates showed no effects on the hydroxyl radical reactions with the model organic contaminants.

Based on these experiments, we moved forward by preparing laboratory solutions containing the interfering species most commonly found in natural waters and wastewaters: bicarbonate and DOM or natural organic matter (NOM). Levels of bicarbonate/carbonate and DOM differ considerably in natural bodies of water but are always present to some degree. Both dissolved species have the potential to initiate different chemical pathways and alter the overall efficiencies of the hydroxyl radical reactions with contaminant chemicals.

4.2.1 Bicarbonate/Carbonate

Both bicarbonate and carbonate react readily with the hydroxyl radical to produce the carbonate radical anion, $CO_3^{\bullet -}$ (Buxton et al., 1988; Weeks and Rabani, 1966). At typical natural or wastewater solution pH, the predominant species is the bicarbonate ion. The hydroxyl radical-induced oxidation of either dissolved substance produces the carbonate radical anion as the product, but it forms at a much higher rate when the carbonate ion reacts with the hydroxyl radical:

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad pK_a = 10.69 \qquad [4\text{-}1]$$

$$^{\bullet}OH + HCO_3^- \rightarrow CO_3^{\bullet -} + H_2O \qquad k = 8.5 \times 10^6\ M^{-1}s^{-1} \qquad [4\text{-}2]$$

$$^{\bullet}OH + CO_3^{2-} \rightarrow OH^- + CO_3^{\bullet -} \qquad k = 3.9 \times 10^8\ M^{-1}s^{-1} \qquad [4\text{-}3]$$

The $CO_3^{\bullet -}$ radical is a reactive species that can also oxidize organic compounds (Behar et al., 1970; Busset et al., 2007; Canonica et al., 2005; Huang and Mabury, 2000; Mazellier et al., 2007). It is different from the hydroxyl radical in that it reacts mainly by electron or hydrogen atom transfer and with a wide range of rate constants (Neta et al., 1988). At higher concentrations, bicarbonate/carbonate can intercept hydroxyl radicals and create different radical reaction pathways. Therefore, it is important to assess the reaction efficiencies of the selected organic contaminants in the presence of typical wastewater concentrations of these species (Table 4.1).

4.2.2 DOM/NOM

DOM influences hydroxyl radical reactions, since the vast majority of organic compounds are susceptible to attack by this strong oxidant. At the very least, DOM is expected to compete with other dissolved organic contaminants for the hydroxyl radical. Therefore, the impacts of DOM on the oxidation of microcontaminants need to be quantified. Typical secondary-treated wastewater concentrations of DOM (usually reported as TOC) are expected to fall in the 5- to 30-ppm range; therefore, a 10-ppm total carbon concentration was selected as a baseline value for most of our experiments.

DOM reacts readily with the hydroxyl radical. Recently, the average rate constant for DOM was reported as 2.2×10^8 M (as C)$^{-1}$ s^{-1} (Westerhoff et al., 2007). DOM radicals were found to exist long enough to promote or stabilize slower radical reactions. The exact effects of the DOM will be dependent upon the type of DOM present, and much of the chemistry of this broadly defined dissolved matter is unexplored. To minimize the impact of this variability, we used characterized Suwannee River DOM and Fulvic Acid Standard II, as purchased from the International Humic Substances Society, for our model solution studies in this project.

4.3 TREATED WASTEWATERS

Since most of the treated wastewaters used in the project were supplied from Orange County, only the parameters from these waters will be discussed. Table 4.1 summarizes the typical treated wastewater samples utilized in the radiolysis studies. Table 4.2 summarizes measured information on the aforementioned important dissolved substances: bicarbonate and DOM.

Table 4.1. Wastewater and Laboratory Solutions: Descriptions, Selected Parameters, Measured Removal Constants, and Efficiencies

Abbreviation	Water Description	pH range
UVP	Advanced oxidation product containing H_2O_2; most extensively treated wastewater	6.1–6.5
ROP	Reverse osmosis permeate	5.7–6.7
MFE	Microfiltration effluent; chlorinated prior to the filtration	6.8–8.0
Q1 (least treated)	Secondary treated wastewater; no disinfection (no chlorine)	7.5–8.2
MilliQ Water	--	7.0
DI Water + DOM	Suwannee River fulvic acid, fulvic acid, 10 ppm	4–5.5
DI Water + $NaHCO_3$	10 mM $NaHCO_3$	7–10
DI + DOM + $NaHCO_3$	10 ppm of SRFA, 10 mM $NaHCO_3$	7–8.5

Table 4.2. Treated Wastewaters (from May 28th, 2008 Samples) and Important Parameters[a]

Water Type	Value for: pH	TOC (mg/L)	HCO_3^- (mg/L)	CO_3^{2-} (mg/L)
Q1	7.8	16.1	375	<0.6
MFE	7.9	13.3	371	<0.6
ROP	6.5	0.16	19.5	<0.6
UVP	6.6	0.17	16.8	<0.6

[a]From Ken Ishida of the Orange County Water District.

4.4 EXPERIMENTAL PROCEDURES

Most chemicals used in this study were obtained from the Aldrich Chemical Co. at the highest purity available and were used as received. Solutions were made using water filtered by a Millipore Milli-Q system or in the supplied treated wastewaters (Table 4.2). The Q1 samples were filtered as needed to remove suspended solids. During the dates of irradiation, the average dose rate was 0.0441 kGy min^{-1}.

Dilute solutions (range, 1 to 500 µM) of the selected organic compounds were prepared in deionized water solutions, laboratory-prepared solutions, and treated wastewater samples. Water solutions were saturated with $N_2O(g)$ to provide oxidative conditions only, since the aqueous electrons and hydrogen atoms produced in the radiolysis are converted to hydroxyl radicals by N_2O (equations 2.3 and 2.4 [Chapter 2]). In a few experiments, solutions were saturated in a 4:1 ratio of N_2O and O_2 to more accurately mimic natural oxidative conditions.

The samples were irradiated for selected times/radiation doses, and the changes in concentration of the organic contaminants were followed using HPLC. A Waters HPLC system (Millennium 2010, Waters 717 plus Autosampler, Waters 600 Controller Solvent Pump) equipped with a Supelco Discovery® C_{18} column (5 µm; 250 mm × 4.6 mm) was utilized. For BPA analyses, a solvent flow of 0.85 mL min^{-1} employed three solvents: water, methanol, and dilute acetic acid solution (1%). The initial solvent mixture consisted of 70% methanol and 30% water. Through use of a gradient curve, the solvent mixture was changed to 30% methanol, 68% water, and 2% acetic acid solution at the 13-min mark. The solvent switched back to the original flow by 16 min. The solvents and gradients were adjusted as necessary for other organic compounds and oxidation products. A photodiode array detector monitored the 200- to 400-nm range. Once the HPLC data were graphed, the removal constant and efficiency of the hydroxyl radical with the compound under the specified conditions were determined. When relevant, products of the oxidative transformations were noted and identified by known compound analysis or by LC/MS.

4.5 RESULTS AND DISCUSSION

4.5.1 BPA

The results from an extensive matrix of experiments in which BPA served as a model organic contaminant are summarized in Table 4.3. BPA was the original compound tested and was used as a surrogate throughout the project. Several interesting findings emerged from experiments with aqueous BPA solutions. In the early experiments of this project, the concentration of BPA utilized was typically 0.5 mM. While this concentration is far greater than that expected in wastewaters, the work enabled us to understand the need to determine the efficiencies of the model compounds with the hydroxyl radical without interference from reaction intermediates.

Once the understanding of appropriate radiation dose and of contaminant concentration was established, most of the remaining experiments with BPA were done on the level of 50 µM. Whenever a set of experiments was performed with BPA, the baseline BPA in deionized water was part of the experiment to ensure consistency in the experimental protocol. Solutions of BPA were prepared with the treated wastewaters, and the removal constants and efficiencies were determined. This information is listed in Table 4.3 and shows the significant loss of hydroxyl radical efficiency with the less-treated wastewater. It becomes quite obvious that the dissolved substances present in the Q1 and MFE treated wastewaters adversely affect potential AOP applications.

Table 4.3. Removal Constants and Efficiencies from the Gamma Radiolysis of BPA Solutions in Treated Wastewaters and Deionized Water and with Different Levels of Sodium Bicarbonate

BPA Solution	Removal Constant, µM/kGy	Efficiency (%)
50 µM BPA (DI)	0.46 ± 0.04	78
50 µM BPA in UVP	0.45 ± 0.04	76
50 µM BPA in ROP	0.45 ± 0.03	76
50 µM BPA in MFE	0.25 ± 0.03	42
50 µM BPA in Q1	0.20 ± 0.01	34
50 µM BPA + 10 mM $NaHCO_3$	0.35 ± 0.02	59
50 µM BPA + 100 mM $NaHCO_3$	0.39 ± 0.03	66
50 µM BPA + 500 mM $NaHCO_3$	0.46 ± 0.03	78

The average removal constant for BPA in deionized water was determined to be 0.46 ± 0.04, corresponding to a hydroxyl radical degradation efficiency of 78%. Figure 4.1 is a sample graph of the data for the removal constant determination. In the presence of bicarbonate ions, removal constants and reaction efficiencies decrease. The average value for the destruction of BPA in the presence of 10 mM $NaHCO_3$ is 0.35 ± 0.02, corresponding to an efficiency, 59%, significantly lower than the destruction of BPA by $^{\bullet}OH$ in pure water.

At higher bicarbonate concentrations (100 or 500 mM), the removal constant and efficiency "recovered" to a level of $^{\bullet}OH$ efficiency similar to that realized for BPA in deionized water. At the very high concentration of 500 mM $NaHCO_3$, bicarbonate is able to totally outcompete the organic contaminant for the hydroxyl radicals. Therefore, under these conditions, only carbonate radicals oxidatively transform the BPA. According to the experimental data, the carbonate radicals react differently (via initial electron transfer) yet are as efficient as the hydroxyl radicals in the oxidative degradation of BPA.

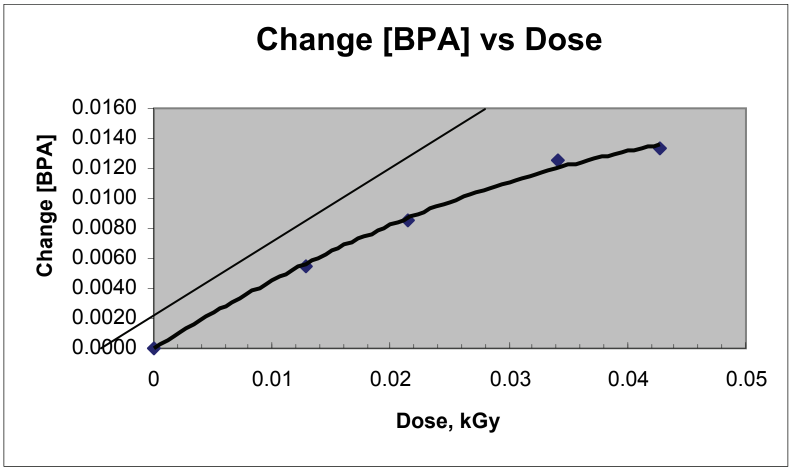


Figure 4.1. Change in concentration of BPA plotted against applied radiation dose in kGy. The removal constant is defined as the initial slope (straight line) of the curve.

Based on the average amount of TOC in the Orange County treated wastewater samples, we utilized 400 µM DOM or 10 ppm (Suwannee River fulvic acid) in our lab-prepared solutions experiments. A solution of 50 µM BPA with 400 µM DOM was irradiated and analyzed; the removal constant for these conditions, 0.42 ± 0.03, was slightly lower than the 50 µM BPA in deionized water (0.46 ± 0.04). Furthermore, the hydroxylated BPA product was readily apparent and to a greater extent in these HPLC analyses, confirming the presence of the same reaction mechanism observed for the hydroxyl radical with BPA in pure water.

If the DOM functioned solely as an $^{\bullet}$OH scavenger, the predicted removal constant for BPA would be approximately 0.38, in comparison with the experimental value of 0.42, based on the concentrations and rate constants of BPA and DOM. The experimental removal constant is slightly higher than expected, possibly indicating that DOM radicals are also able to participate in the oxidative breakdown of BPA.

After the individual effects of these two major dissolved species were quantified, experiments were performed to determine any synergistic effects of bicarbonate and DOM. A solution containing 50 µM BPA, 10 mM $NaHCO_3$, and 10 parts of DOM per millionwas prepared and saturated with N_2O. The solution pH was measured as 8.4. After gamma irradiation of the solution at specific doses, a substantial decrease in the oxidative degradation of BPA resulted. A similar solution was prepared, but the pH was adjusted to approximately 7 using perchloric acid, and again the removal constant was considerably lower than the values figured for the other laboratory-prepared solutions. The removal constants and efficiencies averaged from three different experimental sets are shown in Table 4.4.

Individually, dissolved DOM and HCO_3^- did not significantly lower the BPA/$^{\bullet}$OH removal constant/hydroxyl radical efficiency. Although the moderate bicarbonate concentrations (10 mM) did reduce the efficiency of the BPA + $^{\bullet}$OH reaction through some type of modification of the mechanism of oxidative degradation, the removal constant for BPA and $NaHCO_3$ (0.37) was not as low as the removal constants of the less-treated wastewater samples, Q1 and MFE (0.20 and 0.25).

However, when both bicarbonate and DOM were added to the 50 μM BPA solution at the unadjusted pH (~8.4) of this solution, the average removal constant was determined to be 0.15, a value drastically lower than those associated with solutions containing each individual component. When the 50 μM BPA solution was prepared again with both DOM and bicarbonate and the pH was adjusted near neutrality, the removal constant was again noticeably low (0.22) but not as low as that of the pH 8.4 solution.

Table 4.4. Removal Constants for BPA in Various Solutions and Measured pH Values

BPA Solution	**Removal Constant (μM/kGy)**	**pH**
50 μM BPA in DI water	0.46 (± 0.04)	8.5
50 μM BPA + 10 mM $NaHCO_3$	0.35 (± 0.02)	8.4
50 μM BPA + 400 μM DOM	0.42 (± 0.03)	5.5
50 μM BPA + 400 μM DOM + 10 mM $NaHCO_3$	0.15 (± 0.01)	8.4
50 μM BPA + 400 μM DOM + 10 mM $NaHCO_3$	0.22 (± 0.02)	7.0
50 μM BPA in Q1 wastewater	0.20 (± 0.01)	7.8
50 μM BPA in MFE wastewater	0.25 (± 0.03)	7.6

The experimental aqueous solutions irradiated throughout this project were saturated with nitrous oxide gas for maximum hydroxyl radical production. To better mimic natural hydroxyl radical reaction conditions, a 4:1 mixture of N_2O and O_2 was utilized with several of the solutions. The results of these experiments are displayed in Table 4.5. In all cases, the removal constant diminished only to a small extent. The yield of the hydroxyl radicals remains the same (0.56 μmol/Gy) when oxygen is present, and the yield of $^{\bullet}HO_2/O_2^{\bullet -}$ is negligibly small (~0.06 μmol/Gy). This $^{\bullet}OH/O_2$ mixture potentially allows for the following additional stabilization reaction to occur:

$$^{\bullet}\mathrm{OH} + \mathrm{BPA} \rightarrow {}^{\bullet}\mathrm{OH\text{-}BPA} + \mathrm{O_2} \rightarrow \mathrm{BPA\text{-}OH} + \mathrm{HO_2}^{\bullet} \qquad [4\text{-}4]$$

Table 4.5. Bisphenol A Removal Constants for N_2O/O_2 (4/1) Saturation

Solution	**Removal Constant: N_2O/O_2 (4/1) $\mu M\ kGy^{-1}$**
BPA, 50 μM in deionized water	0.42 ± 0.01
BPA, 50 μM + 10 mM $NaHCO_3$	0.22 ± 0.01
BPA, 50 μM + 400 μM DOM	0.39 ± 0.03
UVP	0.43 ± 0.03
ROP	0.42 ± 0.03
MFE	0.22 ± 0.01
Q1	0.20 ± 0.02

Finally, the radiation doses emitted from the gamma sources are too high to allow for accurate experiments with concentrations much lower than 20 μM. Several experiments were performed with 1 μM solutions of BPA, with an alcohol scavenger added to intercept a large percentage of the hydroxyl radicals. Unfortunately, the experimental conditions were not fully optimized before completion of the project.

The following points summarize the main findings of the experiments performed with BPA. A recently submitted paper offers more details (Peller et al., in preparation):

- A prominent intermediate, hydroxylated BPA forms. It is somewhat stable, since a low buildup is noted in the HPLC data.
- The hydroxylated BPA intermediate is more prominent in the presence of DOM and does not form in the presence of bicarbonate.
- DOM had very little effect on the efficiency of the hydroxyl radical's reaction with BPA.
- The lowered efficiency of the BPA + $^{\bullet}OH$ reaction in the presence of both DOM and bicarbonate was more than an additive effect.
- The removal constant determined for the BPA with the hydroxyl radical in the secondary treated wastewater (Q1) was similar to the removal constant determined for the combination of DOM and bicarbonate.

4.5.2 Sulfa Drugs: Sulfamethazine and Sulfamethizole

When sulfamethazine was used as the model organic contaminant, a pattern of hydroxyl radical reactivity similar to that seen for BPA was found. Sulfamethazine was one of the four sulfa drugs studied in the earlier part of the project, the results for which were reported in Chapter 3 (Mezyk et al., 2007). A noteworthy observation is that the oxidative destruction of sulfamethazine by the hydroxyl radical is less effective than that by BPA. The average efficiency of this reaction in pure water was only 47%, compared to the 78% efficiency figured for the BPA. According to these data, only about half of the hydroxyl radicals promote oxidative destruction of the sulfa drug. In the presence of 10 mM sodium bicarbonate, the efficiency drops to 29% but again "recovers" somewhat at higher bicarbonate concentrations.

Table 4.6 summarizes project data on the hydroxyl radical-mediated destruction of sulfamethazine for solutions of sulfamethazine in the range of 41 to 200 µM in deionized water, with various concentrations of bicarbonate solutions, and in treated wastewater solutions. In all cases, the efficiency of the hydroxyl radical in pure water and highly treated wastewater is clearly superior to the hydroxyl radical efficiency in the lower-quality treated wastewater. Also, the removal constants for variations in the sulfamethazine concentration in deionized water (highlighted in gray) are within 0.04, indicating little to no concentration dependence on the removal constant, as predicted. It is worth noting that the experiments utilizing the 41, 79, and 200 µM sulfamethazine solutions were performed only once (either in duplicate or triplicate). (The majority of experiments determining rate constants and efficiencies for this project were run at least three times in duplicate or triplicate.)

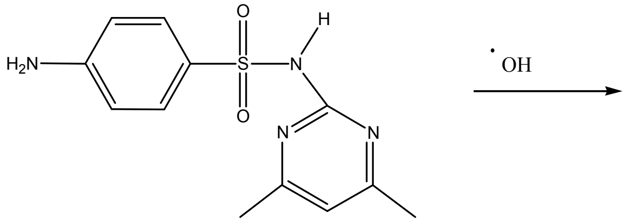


Figure 4.2. Chemical structure of sulfamethazine.

Table 4.6. Removal Constants and Efficiencies for Sulfamethazine Solutions in Deionized Water, in Treated Wastewaters, and with Added Sodium Bicarbonate

Solution Description	Removal Constant, µM/kGy	Efficiency (%)
79 µM sulfamethazine (deionized)	**0.30**	**51**
79 µM sulfamethazine + 10 mM $NaHCO_3$	0.17	29
79 µM sulfamethazine + 50 mM $NaHCO_3$	0.21	36
79 µM sulfamethazine + 100 mM $NaHCO_3$	0.25	42
41 µM sulfamethazine (deionized)	**0.26**	**44**
41 µM sulfamethazine + 10 mM $NaHCO_3$	0.14	24
41 µM sulfamethazine + 50 mM $NaHCO_3$	0.22	37
200 µM sulfamethazine	**0.26**	**44**
50 µM sulfamethazine in RO treated wastewater	0.30	51
50 µM sulfamethazine in MFE treated wastewater	0.17	29
50 µM sulfamethazine in Q1 treated wastewater	0.16	27
50 µM sulfamethazine in BMF (Scottsdale, AZ)	0.14	24

Sulfamethizole, another sulfa drug, was also used as a model compound in the treated wastewaters to examine its behavior according to water quality. The following HPLC chromatograms show the variance in amount of the main oxidation product according to water quality from the earlier experiments when higher concentrations of the organic contaminants were utilized. When a 500 µM sulfamethizole solution in reverse osmosis-level treated wastewater was irradiated for 20 min, corresponding to a dose of 1.78 kGy, 68% of the sulfamethizole was degraded and the area ratio between the sulfamethoxazole and its main oxidation product was 0.47. When a similar solution was prepared in the lower-quality treated wastewater (BMF from the Scottsdale, AZ, Water Treatment Plant), 30 min of irradiation time, corresponding to a dose of 2.67 kGy, was required for the 68% degradation. Furthermore, the area ratio between sulfamethizole and its main oxidation product was only 0.32. The structure of sulfamethizole is shown below.

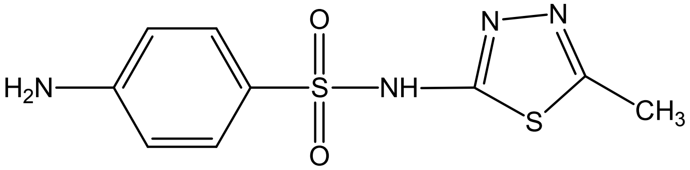


Figure 4.3. Chemical structure of sulfamethizole.

The chromatograms of sulfamethizole are shown in Figure 4.4. The top chromatogram represents the irradiated sulfamethizole in the reverse osmosis-treated wastewater, and the bottom chromatogram represents the irradiated compound in the BMF-treated wastewater. The first major peak on the chromatogram is the oxidation product of sulfamethizole, and the larger, second peak is the sulfamethizole.

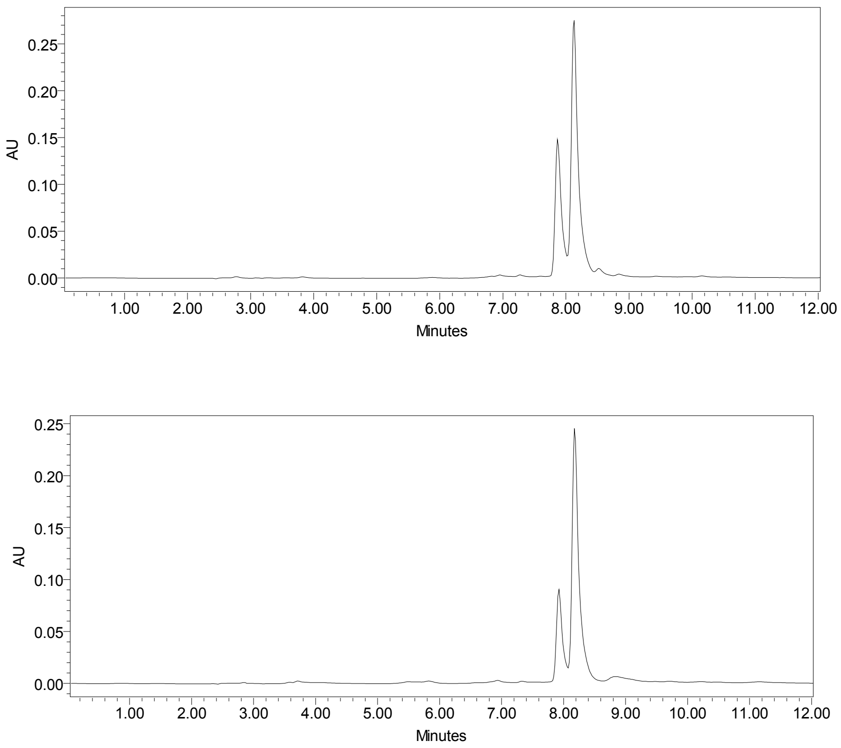


Figure 4.4. Chromatograms of sulfamethizole.

4.5.3 DEET

The organic contaminant known as DEET is *N*,*N*-diethyl-*meta*-toluamide, the most common component of insect repellents, and its structure was shown earlier in this text (see Figure 3.6).

Several 50 µM solutions of this water contaminant were irradiated to realize approximately 20% hydroxyl radical-mediated degradation in order to determine the removal constants and $^{\bullet}$OH efficiencies. The experiments were performed with the treated wastewaters in a few select laboratory-prepared solutions. The values are summarized in Table 4.7 and notably indicate 100% hydroxyl radical efficiency in pure water and 95% efficiency in the reverse osmosis-treated wastewater.

Table 4.7. Removal Constants and Efficiencies for DEET Solutions (~50 μM) in Deionized Water, in Treated Wastewaters, and with Added Sodium Bicarbonate and DOM

Water Solution	Removal Constant, μM/kGy	Removal Efficiency
Deionized water	0.60	**100%**
10 ppm DOM	0.50	85%
5 mM $NaHCO_3$	0.48	81%
10 ppm DOM + 5 mM $NaHCO_3$	0.39	66%
RO-treated wastewater	0.56	95%
MFE-treated wastewater	0.25	42%
Q1-treated wastewater	0.25	42%

In the hydroxyl radical oxidations of BPA with both $NaHCO_3$/DOM present, lower-than-expected removal constants were obtained, indicating a synergistic effect of the dissolved species in removing hydroxyl radicals. The data collected using the organic contaminant DEET, on the other hand, appear to show a simple additive effect of these dissolved substances. The complete effectiveness of the hydroxyl radical in its reaction with DEET diminished by approximately 20% in the presence of DOM. When the hydroxyl radical oxidation of DEET took place in the presence of 5 mM $NaHCO_3$, a similar decrease in the effectiveness (~20%) of the oxidation was realized. With both dissolved species present, the expected 40% decrease was determined, suggesting an additive effect.

Another important point to emphasize in the hydroxyl radical-mediated destruction of DEET is the absence of any persistent intermediates upon HPLC analyses. This point seems to indicate that the oxidized intermediates formed in the reaction pathway are as readily oxidized as the DEET, which is efficiently degraded. At the low concentrations in both pure water and water solutions containing dissolved species, the reaction proceeds without the buildup of intermediates. Different from the BPA and sulfamethazine experiments, the removal constants determined for DEET in the less-treated wastewater solutions, MFE and Q1, are significantly lower than the removal constant determined for DEET with both DOM and $NaHCO_3$. However, caution must be applied to the interpretation of these data: these experiments need to be repeated to verify our given results. The values in Table 4.7 represent only one set of data.

4.5.4 Caffeine

Caffeine was used as a model organic contaminant early in the project when the experiments employed concentrations in the realm of 0.5 mM. Caffeine is shown in Figure 4.5.

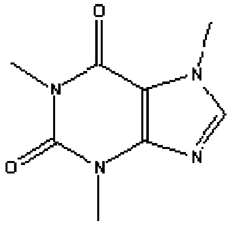


Figure 4.5. Chemical structure of caffeine.

As expected, the hydroxyl radical removal efficiency for caffeine was diminished in line with water quality as noted in Figure 4.6 below, which was first presented earlier in this study. More recently, a set of experiments employing lower concentrations of caffeine, ~50 µM, was conducted in the last received samples of treated wastewater; unfortunately, experiments to determine the effects of the individual dissolved species were not conducted as the project came to a conclusion before these experiments could be run. Our preliminary results from the caffeine in the treated wastewaters are shown in Table 4.8.

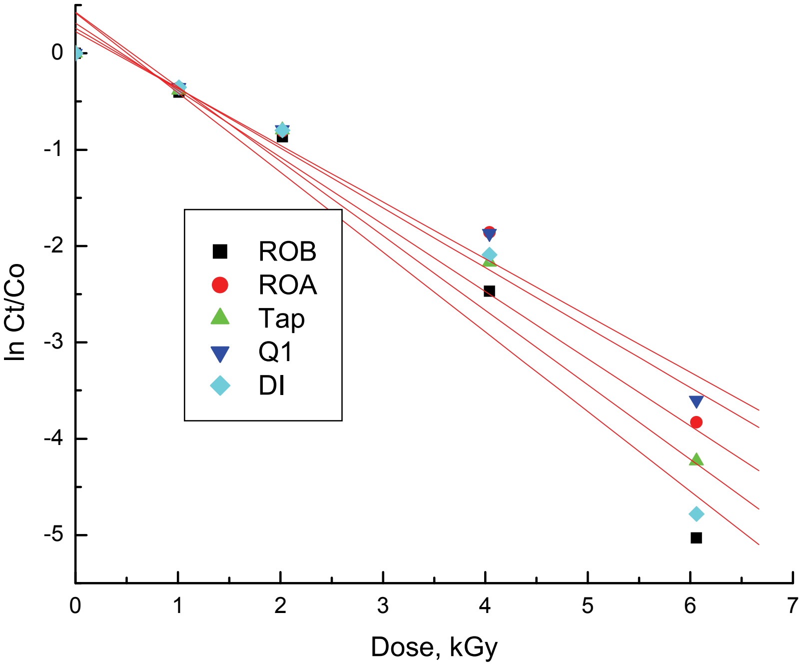


Figure 4.6. Oxidative degradation of caffeine in deionized water, tap water, and 3 treated wastewaters of differing quality (ROB, ROA, and Q1, in order of decreasing quality).

Table 4.8. Hydroxyl Radical Removal Constants and Efficiencies for the Compound Caffeine (~50 µM)

Water Solution	Removal Constant	Removal Efficiency (%)
Deionized water	0.48	81
RO-treated wastewater	0.47	80
MFE-treated wastewater	0.15	25
Q1-treated wastewater	0.10	17

Again, these experiments on caffeine dissolved in the treated wastewaters need to be repeated, especially as the removal constants generated from the gathered data were much lower than expected. While the efficiency of the hydroxyl radical appears to be quite good in the deionized water and the highly treated RO wastewater, ~80%, this degradative oxidation is highly impeded in the lower-quality treated wastewaters, according to this one set of data.

4.6 CONCLUSIONS

An important conclusion from this component of our project is that in the treated wastewaters specific dissolved substances, HCO_3^- and DOM, can have notable effects on the hydroxyl radical reaction pathways with organic contaminants. For example, in the sulfamethizole oxidation, the prominent oxidative degradation intermediate does not form to the same extent in the lower-quality waters as it does in the purer water solutions; the altered reaction pathway is even more evident in the experiments with BPA, where the oxidized intermediate does not form at all. The hydroxylated BPA oxidized product would be indicated by HPLC peaks, so no peaks indicate no formation of oxidized intermediates in the lower-quality treated wastewaters or in the solutions containing a 10 mM concentration or greater of bicarbonate.

Many experiments were performed with BPA (or sulfamethazine) in solutions with various concentrations of bicarbonate. The results of these sets of experiments suggest that an alternative degradation pathway exists in the presence of the bicarbonate ion (concentration dependent), which may lead to a slightly lower removal of the organic contaminant. DOM, a common constituent of natural waters, reacts readily with the hydroxyl radical; however, when examined in the absence of bicarbonate ion, the DOM did not seem to alter the removal efficiencies of the organic contaminants to any great extent.

When both bicarbonate and DOM were added to BPA solutions and subjected to radiolysis under N_2O-saturated conditions, a drastic change in oxidative degradation efficiency was observed. This work, which tested the effects of the bicarbonate and DOM both separately and in combination, was extended to the compounds sulfamethazine and DEET in the last 2 months of the project, but these two latter contaminants showed somewhat different results. In the experiments with BPA, the overall effect of both dissolved species is more than just an additive effect. On the other hand, the experiments employing DEET as the organic contaminant indicate the combination of the dissolved species is likely an additive effect.

To determine the extent of these patterns of reactivity of organic contaminants with the hydroxyl radical, more experiments involving DOM, bicarbonate and treated wastewaters need to be performed on a variety of organic contaminants of both similar and different chemical structures. Radiation chemistry techniques are uniquely useful for the study of these hydroxyl radical reactions at concentrations around 50 μM, and the potential exists to study the reactions at much lower concentrations with the use of a radical scavenger.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The original proposal goals were to:

- Determine reaction rates of 30 to 50 target chemicals with hydroxyl radicals, $^{\bullet}OH$, and hydrated electrons, e^-_{aq}.
- Elucidate destruction mechanisms for five selected target compounds representative of broader classes of organic microconstituents.
- Determine the free radical destruction of BPA in waters of different quality.

In addition to fulfilling all of these goals and in fact surpassing the second one, our findings allow us to make the following additional conclusions/observations:

(1) Radiation chemistry is one of the most versatile methods of studying the fundamental free-radical chemistry of these chemical contaminants. In this project we have optimized measurement techniques that have allowed us to efficiently obtain quantitative data for radical reaction kinetics and degradation efficiencies in both pure and real-world waters.

(2) The kinetics of the hydroxyl radical and hydrated electron with the target chemicals are fairly consistent and not very dependent upon the contaminant structure. The hydroxyl radical oxidation occurs quickly, with rate constants on the order of 10^9 M^{-1} s^{-1}. The hydrated electron reduction rate constants were in the range of 10^8 to 10^{10} M^{-1} s^{-1}. These large values suggest that radical treatment of chemically contaminated waters by AOPs could be feasible.

(3) In addition to reaction rate constants, the concept of reaction efficiency is an integral component for the ultimate application of free-radical processes in water reuse. The effectiveness of a particular radical in destroying a chemical contaminant ranges from zero to 100% and needs to be included with the reaction rate constants when AOP technologies are being considered for water treatment.

(4) The investigations of radical reactions in pure water may not be directly applicable to waters containing DOM and bicarbonate, such as treated wastewaters and natural waters. For some chemicals, a synergistic effect that drastically decreased the degradation efficiency was found, while for others, only an additive effect that could be predicted by standard competition kinetics was seen.

5.2 RECOMMENDATIONS

The issue of quantitative pharmaceutical removal from water, wastewater, and natural waters remains a major public concern. As such, it is essential to carefully select the most relevant chemical contaminants for these types of study. Our contaminant prioritization was based on two compilations, which listed the top 200 name-brand drugs and the top 200 generic drugs by sales volume for 2007. The underlying premise is that those that are the highest in sales volume are likelier to be encountered in the environment.

As this work barely scratched the surface, we have the following recommendations for continued effort in this area. We consider implementation of them necessary for the full evaluation of AO/RPs for the removal of chemical contaminants from waters:

(1) Major efforts need to be conducted to identify the stable by-products of these radical reactions with the main pharmaceuticals of interest. Although a daunting task, it is critical to determine these species so that both quantitative destruction mechanisms and toxicity data can be obtained and incorporated into computer models of these treatment AOPs.

(2) While kinetic parameters and degradation efficiencies can be measured if pure compounds can be isolated, such data may be more difficult to obtain for reaction by-products. Therefore, an alternative approach to determining these parameters is to use ab initio computational methods. These methods can be benchmarked against quantitative experimental data obtained in both pure and real waters.

(3) Significantly more experimental work using natural waters of different quality and chemical composition needs to be performed for a complete understanding of the AOP treatment of contaminant chemicals. It is important that these studies also include measurements for species concentrations that are similar to those found at real-world treatment levels and that quantitative correlations between measured water quality parameters and reaction efficiencies be made.

(4) The evaluation of biological activity of AOP-treated chemically contaminated waters needs to be performed. These studies are essential for EPOCs and for the parent compounds that have known biological effects.

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WATEREUSE
FOUNDATION

1199 North Fairfax Street, Suite 410
Alexandria, VA 22314 USA
(703) 548-0880
Fax (703) 548-5085
E-mail: Foundation@WateReuse.org
www.WateReuse.org/Foundation