Summer 8-13-2014

Mechanisms and transients involved in the solar conversion of petroleum films in aquatic systems

Phoebe Z. Ray
pzray@uno.edu

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Mechanisms and transients involved in the solar conversion of petroleum films in aquatic systems

A Dissertation

Submitted to the Graduate Faculty of the University of New Orleans
In partial fulfillment of the
Requirements for the Degree of

Doctor of Philosophy
In
Chemistry

By
Phoebe Ray

M.S. University of New Orleans, Louisiana, 2014
B.S. University of South Florida, Florida, 2007
A.A. St. Petersburg College, 2004

August 2014
Dedicated to my husband, James Ray and our son, Grant Ray.

My parents,
Charles and Patricia Zito,
My brother Nick Zito,
My sister Aislinn Stone,
My In-Laws,
Don and Susan Ray, John and Danielle Ray, Eric and Nicole Ray.

Without all of your support, I would not have been able to set my goals so high and accomplish so much. For that I am forever grateful.
I want to express my deepest gratitude to my husband, James Ray, for his never-ending support and inspiration throughout my entire career in Chemistry. Thank you to my father, Charles Zito, for thinking I could do anything. You have always supported my decision to further my education. During my undergraduate career, you gave your last dollar to help contribute toward my tuition. To my stepmother, Patricia, and my stepsister, Aislinn, thank you for being there during the toughest times. And finally, Don and Sue Ray for believing in me.

A very special thanks to my boss and advisor, Dr. Matthew A. Tarr, for all the guidance, and support you have given me. Your support and passion for the field has inspired me to become a better scientist and has helped me realize my dreams and future goals. You have made it possible for me to see parts of the world I would have never traveled to on my own. I was able to present my research in Japan, Colombia, and around the United States. This travel experience allowed me to gain perspective on the type of research being conducted by international scientists. You introduced me to Nobel Laureates and many collaborators who share the same interests and research goals. I am honored to have worked with you and I could not have asked for a better advisor.

A special mention to Dr. Amy McKenna, from the National High Magnetic Laboratory at Florida State University, for introducing me to the world of Petroleomics and FT-ICR MS. Dr. McKenna’s knowledge and brilliance in the field inspired me to become a better scientist. Through her I met two other great scholars, Dr. Huan Chen and Dr. David Podgorski, both of whom were motivating and contributed greatly to my research. I also want to acknowledge Dr. Paul Dunk and Stephen Rowland for their kindness and friendship at the Maglab. A special thanks to Dr. Alan Marshall for providing the ICR facility and user program which allows graduate students like myself to conduct research at the MagLab. The User program, funded through NSF, allowed me to use one of the best instruments in the world for petroleum analysis. Thanks to Dr. Christopher Reddy, Bob Nelson and Dr. Christoph Aeppli from Woods Hole Oceanographic Institute for the GC-GC and TLC-FID work. Dr. Ed Overton from LSU, thank you for your contribution for the GC-MS work on biomarkers. I would also like to express my gratitude to my committee members, Dr. John Wiley, Dr. Mark Trudell, and Dr. Yang Cai for their comments and suggestions throughout my graduate research. Thank you to Dr. Richard
Cole and Dr. Syeda Quadri for their help and guidance with Mass Spectrometry.

I would like to extend my gratitude toward my undergraduate protégés who helped contribute toward my research. They are Amy Olson, Jeremy Stroud, Lacie Duplessis, Shaniqua Hayes, Joana Franco, and Joseph La. It was such a pleasure to work with each of you.

Thank you to past and present group members for their support. They are Dr. Gayatri Sahu, Dr. Sarah King, Isabella Schmitt, Scott Gordan, Angela Ellender, Richie Provost, Parisa Parini, Ujwal Patel, Kristen Williams, Donna Peralta, Dustin Kountz, Olivia McKenzie, Alex Lyons, Violet Lee and Johnny Avants. Thank you, Adam Nguyen, for your support and friendship throughout this program.

Lastly, I would not have been able to conduct this research without the financial support from funding. Work performed at the National High Magnetic Field Laboratory was supported by NSF Division of Materials Research through DMR-11-57490, BP/The Gulf of Mexico Research Initiative to the Deep-C Consortium, the Florida State University Future Fuels Institute, and the State of Florida. Work performed at the University of New Orleans was supported by NSF (CHE-1111525) and BP/The Gulf of Mexico Research Initiative. BP provided the oil samples used in this study.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AI</td>
<td>Aromaticity Index</td>
</tr>
<tr>
<td>AM</td>
<td>Air Mass</td>
</tr>
<tr>
<td>BA</td>
<td>Benzoic acid</td>
</tr>
<tr>
<td>BP</td>
<td>British Petroleum</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>CDOM</td>
<td>Chromophoric dissolved organic matter</td>
</tr>
<tr>
<td>CH₂</td>
<td>Methylene</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>Da</td>
<td>Dalton</td>
</tr>
<tr>
<td>DBE</td>
<td>Double Bond Equivalence</td>
</tr>
<tr>
<td>DBE-O</td>
<td>Double Bond Equivalence minus Oxygen</td>
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<td>DCM</td>
<td>Dichloromethane</td>
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<td>DOM</td>
<td>Dissolved Organic Matter</td>
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<td>DWH</td>
<td>Deepwater Horizon Oil</td>
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<tr>
<td>ESI</td>
<td>Electrospray Ionization</td>
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<tr>
<td>FFA</td>
<td>Furfuryl Alcohol</td>
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<tr>
<td>FT-ICR MS</td>
<td>Fourier transform ion cyclotron resonance mass spectrometry</td>
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<tr>
<td>GC</td>
<td>Gas chromatography</td>
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<tr>
<td>GW</td>
<td>Gulf of Mexico water</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
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<tr>
<td>HH</td>
<td>Haag and Hoigné Model</td>
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<tr>
<td>HFO #1</td>
<td>Heavy Fuel Oil-SRM 2717a</td>
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<tr>
<td>HFO #2</td>
<td>Heavy Fuel Oil-SRM 1622e</td>
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<tr>
<td>HFO #3</td>
<td>Heavy Fuel Oil-SRM 1620a</td>
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<tr>
<td>H₂SO₄</td>
<td>Sulfuric Acid</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition/ExPLANation</td>
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<tr>
<td>--------------</td>
<td>-----------------------------------</td>
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<tr>
<td>ICR</td>
<td>Ion Cyclotron Resonance</td>
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<tr>
<td>k′i</td>
<td>First order Rate Constant</td>
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<td>kilojoule</td>
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<td>NIST</td>
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<td>NP</td>
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<td>Transmission Electron Microscope</td>
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<td>TiO₂</td>
<td>Titanium dioxide</td>
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<td>V</td>
<td>Volt</td>
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<td>v</td>
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xiii
VAN  NIST 8505 vanadium crude
W    Watt
WDWH Weathered Deepwater Horizon Oil
WSO  Water Soluble Organics
ZM   Zhou and Mopper Model
ZnO  Zinc oxide
6-HP-ONE 6-hydroxy(2H)pyran-3(6H)-one
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Table 3.4. Formation rate of HO, pseudo first order rate constant for scavengers in the oil/water system, and steady state concentration of HO for several oil/water systems. Uncertainty in F_{HO} and k’s were typically 30%. For [OH]_{SS}, reported error is one standard deviation for 3 to 6 measurements. 120 µL of surface oil containing oxide was placed over 10 mL of water containing varying concentrations of BA and irradiated for 3 h at 1.2 times solar noon intensity (AM 1.5) in a jacketed beaker maintained at 27°C.

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Table 7.1. API and elemental composition for each oil.
ABSTRACT

The behavior of Deepwater Horizon crude oil and other sources of oil were investigated when exposed to sunlight in aquatic systems under environmentally relevant conditions. This research decoupled the abiotic and biotic weathering modifications of oil by focusing solely on the photochemical transformations of oil in aquatic systems. Photochemical rates and mechanisms were measured through the determination of reactive transients. Total hydroxyl radical formation was studied using high benzoic acid concentrations and varying exposure time. Titanium dioxide (TiO$_2$) nanomaterials were added to the system in an effort to determine if the photocatalyst would enhance oil photodegradation. Photochemical production of singlet oxygen from thin oil films over seawater and pure water was measured with furfuryl alcohol as a selective chemical probe. The loss of furfuryl alcohol and the formation of 6-hydroxy(2H)pyran-3(6H)-one were monitored. Photochemical production of organic triplets from 6 different compositions of petroleum was measured through the cis-trans isomerization of 1,3 pentadiene in Gulf water. The data correlate very well with previously measured singlet oxygen concentrations. The energies were measured in the range of 280-300 kJ/mol. Macondo Well Oil from the Deepwater Horizon (DWH) rig was mixed with pure water and seawater and irradiated with simulated sunlight. After irradiation, the water-soluble organics (WSO) from the dark and irradiated samples were extracted and characterized by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Liquid-liquid extraction yielded two fractions from dark and irradiated water/oil mixtures: acidic WSOS (negative-ion electrospray (ESI)), and base/neutral WSOS (positive-ion ESI). These fractions were analyzed by FT-ICR MS to catalogue molecular-level transformations that occurred to oil-derived WSOS after solar irradiation. The increased abundance of higher-order oxygen classes in the irradiated samples relative to the dark samples indicates that photooxidized components of the Macondo crude oil become water-soluble after irradiation. Time series studies were performed to observe the changes in WSO composition. The predominance of higher-order oxygen classes indicates that multiple photochemical pathways exist that result in oxidation of petroleum compounds. More oxygenated compounds were observed in the WSO acid fraction of oils with higher API gravity.

Keywords: Oxygenated Compounds, Photochemistry, Petroleum, Reactive Transients, TiO$_2$, Deepwater Horizon
CHAPTER 1. BACKGROUND

INTRODUCTION

*Deepwater Horizon Oil Spill*

Photochemical transformation of intact crude oil has been studied to a limited extent over the last 40 years. In April of 2010, the platform, *Deepwater Horizon*, was destroyed as a result of an explosion. As a result, 4.9 to 5.8 million barrels of oil spilled into the Gulf of Mexico\(^2\). This oil spill was the largest in the history of the United States (See figure 1.1), creating a disruption of an entire ecosystem.

![NASA satellite image of the Deepwater Horizon Spill site.](image)

*Figure 1.1. NASA satellite image of the Deepwater Horizon Spill site.*
Despite numerous studies of the spill\textsuperscript{2-10}, many short and long term impacts of the oil spill are poorly understood.

**Photochemistry**

In order for a photochemical reaction to take place, a compound must have the ability to absorb light. This is the first law of photochemistry. Compounds that are able to absorb light are called chromophores. Chromophores have structural moieties that exhibit a characteristic UV/Vis spectrum\textsuperscript{11}. Absorption of light promotes these compounds to their excited state and the electron can move from bonding to nonbonding or antibonding orbitals. The electronic transitions from $\pi$ to $\pi^*$ form the most intense absorption bands\textsuperscript{11}. The second law, called the photoequivalence law, states that only one molecule can absorb a photon of light by a chemical system\textsuperscript{11}. This study focuses on utilizing energy from the solar spectrum to study the photodegradation of petroleum. Figure 1.2 shows an image of the solar spectrum or visible light ranging from about 400 nm to 750 nm. The visible light spectrum is composed of different wavelengths of light, which have different energies.

![Figure 1.2. The solar spectrum](image)

When a molecule accepts a photon, the energy gained causes the molecule to go from its
ground state, \( S_0 \), to its first excited state, \( S_1 \), or a higher energy excited state. The Jablonksi diagram shown in figure 1.3 illustrates these basic principles of photoexcited states.

![Jablonski diagram](image)

**Figure 1.3.** Jablonski diagram (courtesy of D. Kountz)

Once the molecule reaches the first excited state, \( S_1 \), a series of processes can occur. The molecule can go through a series of relaxation processes, which result in a radiationless loss of energy. If the molecule is largely aromatic and conjugated it can convert from a singlet state to a lower energy triplet state (\( T_1 \)), this process being called intersystem crossing.\(^{11} \) The molecule then goes through a series of transitions where the energy is transferred or lost and the molecule returns to its initial ground state. There are two types of photochemical reactions: direct and indirect photolysis. Direct photolysis is when the compound of interest absorbs the photon and subsequently reacts\(^{11,12} \). Indirect photolysis occurs when a species that is not the compound of interest absorbs the light and initiates a series of reactions that result in the transformation of the chemical of interest\(^{11,12} \). This dissertation will focus on these processes when discussing the photochemical reactions that take place as sunlight interacts with
Reactive Transients

In 1975, Hansen reported on the photodegradation of thin films of crude oil fractions on sea water\(^{13}\). Photochemical degradation of PAHs in thin films of spilled oil on rocks were investigated\(^3\). There have been numerous published studies regarding photoproducts produced in natural water from the photolysis of dissolved organic matter (DOM)\(^{14}\). Dissolved organic matter is a group of natural compounds composed of humic substances, which are typically made up of material from dead plants and other organisms after processing in their surrounding environment\(^{15}\). These compounds can generate reactive species through the acceptance of solar energy. Once DOM is exposed to sunlight, the types of reactive transients that are formed, include hydroxyl radical \(\text{HO}^\cdot\)\(^{16}\), singlet oxygen\(^{1,17,18}\), superoxide\(^{19}\), organic radicals\(^{20-22}\) and organic triplets\(^{23}\). Methods for quantitating these transients have been reported\(^{1,16-19,21,22,24,25}\). Since the composition of DOM varies with its environment\(^{15}\), differences in the transients and their functions have been observed\(^{26}\). Because oil has some chromophores that are similar to those in DOM, it is expected that sunlight irradiated oil will produce similar reactive transients. This current study will focus on the use of chemical probes that were previously used for DOM and apply them to detect reactive transients formed from solar irradiated thin oil films in water. The model for DOM was applied to the oil systems due to the fact that crude oil originates from dead plant matter and has some similar chromophores; however, the chemical structures of crude oil are substantially different from those found in DOM. The types of chromophores that are predominant in oil photochemistry are polyaromatic hydrocarbons or PAHs\(^3\). The role of these photochemical transients formed in the presence of thin oil films on water has not been fully explored. Furthermore, the subsequent chemical and biological processes that occur in the aqueous layer when sunlight reacts with oil are poorly understood. In order to better understand these effects when oil is spilled in an aquatic system, the formation and scavenging of hydroxyl radical\(^{27}\), singlet oxygen and excited triplets were studied in oil on water systems under solar irradiation.

**Hydroxyl Radical.** Hydroxyl radical has been previously implicated in the degradation of organic pollutants\(^{14,26}\), as an intermediate in photo-Fenton chemistry,\(^{14,26,28,29}\) and in
photochemistry of natural organic compounds in aqueous environments. In studies conducted as part of this dissertation, the total amount of HO• formation and the steady state concentrations from thin oil films were determined employing similar methods previously reported by Zhou and Mopper. In 1990, Zhou and Mopper measured the production rates and steady state concentrations of photochemically produced HO• in coastal and open ocean waters and freshwaters. Vaughan and Blough measured HO• production rates in the photolysis of fulvic acid solutions in natural water in the presence and absence of dioxygen. All of these pathways involve oxygen and subsequent formation of superoxide. Hydroxyl radical has been shown to be formed through further reaction of superoxide. Blough et al. proposed similar pathways for PAH photochemistry indicating the importance of oxygen.

Although other pathways of hydroxyl radical formation are not precluded, the pathways presented here and by Blough et al are the most likely mechanisms for hydroxyl radical formation from irradiation of oil.

Singlet Oxygen. A kinetic model described by Haag and Hoigné, determined the amount of singlet oxygen produced in water from sunlight irradiated dissolved organic matter using furfuryl alcohol (FFA) as a chemical probe. Singlet oxygen (1O2) is generated from the excitation of ground state triplet oxygen, generally through energy transfer from another excited species. The process occurs when light promotes a chromophore to its first excited state and then a change in the spin state occurs to the lowest triplet state (refer to figure 1.3). When the triplet state transfers energy to ground state oxygen, singlet oxygen is produced. According to Changtong et al, the lifetime of singlet oxygen is short, in the range of 10^-6-10^-2 seconds. Singlet oxygen can produce oxidative transformations of organic pollutants such as phenolic, heterocyclic and olefinic compounds.

Excited Triplets. The production of excited triplets from solar exposure of petroleum was investigated due to the amount of PAHs found in petroleum. Electronically excited states are important because they are capable of reacting with pollutants or with non-pollutant species present in a system. The complex nature of petroleum is similar to DOM and PAHs found in petroleum act as chromophores. PAHs can absorb a photon while in the ground single state (S₀) to be excited to the first singlet state (S₁) (Figure 1.3). This excited singlet state can
relax back to the ground state or undergo intersystem crossing to the first triplet excited state (T1). This mechanism is important for understanding and predicting the oxidation of pollutants in natural waters and can be directly applied to oil systems. The study focused on the photoisomerization of cis-1,3-pentadiene to trans-1,3-pentadiene, similar to the Zepp et al study, in order to measure triplet formation from petroleum as a function of irradiation time.

Due to their short lifetimes, reactive transients are difficult to measure. Their short lifetimes have required the use of a selective chemical probe to detect and quantitate their formation. The use of a selective chemical probe or scavenger allows relatively easy determination of the steady state concentration of a reactive transient. Singlet oxygen was studied utilizing the methodologies and kinetic model developed by Haag and Hoigné to determine the production and steady state concentration of singlet oxygen from thin crude oil films using FFA as a trapping agent. The Zhou and Mopper approach was also used for singlet oxygen to compare both results generated by these two different models. Excited triplet formation was measured through the isomerization of cis-1,3 pentadiene to trans-1,3 pentadiene related to studies performed with DOM by Zepp et al.

Reactive transient research was conducted on the photochemical formation of hydroxyl radical, singlet oxygen and excited triplets from crude oil collected from the Deepwater Horizon oil spill that occurred on April 10, 2010. Additionally, crude oil from other sources, National Institute of Standards and Technology (NIST) and Noonan (NPO) well #586, were investigated for singlet oxygen production and excited triplet formation. Effect of seawater versus pure water matrices was also considered in all cases. Furthermore, this study investigated the effect of photocatalysts on HO• and singlet oxygen formation during solar irradiation. Photocatalysts are a potential method of speeding decomposition of spilled oil, which was our motivation for investigating photocatalyst amended oil. In addition to accelerating overall degradation rates, photocatalysts can change the reaction mechanisms and the products formed. Changes in oil composition and production of photoproducts can exert important influences on oil fate, toxicity, and bioavailability.

The fundamental knowledge (formation rate, scavenging rate, and steady state concentration) generated by this study may translate into better technologies and better protocols for minimizing the negative impacts of an oil spill in an aquatic system. Titanium
dioxide is a low cost, readily abundant, low toxicity material that has potential to enhance oil degradation\textsuperscript{38-45}.

Overall, reactive transient data will help identify low cost, effective remediation strategies in order to better mitigate the harmful effects of an oil spill.

**Photoproducts-Water Soluble Organics (WSO)**

Biodegradation and photodegradation are the two main pathways for oil transformations in aquatic systems. Many studies have reported on the formation of oxygenated petroleum compounds due to these processes. Despite the extensive study of oil spills, there is little literature on the decoupling of these two pathways and there is still a large void in understanding how sunlight affects the fate and transport of oil. To address this void, a detailed molecular level analysis is needed in order to understand the changes that occur to petrogenic molecules. Advanced analytical techniques for the characterization of polar and nonvolatile compounds can identify photochemical transformations that occur to petrogenic molecules at the molecular level. This study utilized a comprehensive technique, Fourier transform ion cyclotron mass spectrometry (FT-ICR MS), to characterize polar and nonvolatile compounds produced as a result of photochemical transformations of petroleum. This study performed initial exposures of DWH in pure water to address the initial analytical challenges of the study, then utilized seawater to target a more environmentally relevant system. Also, other sources of oil were investigated to study the effect of viscosity and API on the fate and transport of oil after exposure. Furthermore, the photochemical behavior of DWH crude was studied as a function of irradiation time in both matrices.

The goal of this project is to gain a fundamental understanding of the behavior of Deepwater Horizon crude oil along with other crude oil sources, when exposed to sunlight under a range of relevant conditions. Relevant tasks include determination of reaction mechanisms, observation of the effects of photocatalyst nanoparticles (e.g. TiO\textsubscript{2}) and production of WSO photoproducts, on the rate, products, and mechanisms of oil exposed to simulated sunlight in or on pure water or sea water.
Dissertation Objectives

The dissertation seeks to address the following objectives:

1) Determine reaction mechanisms for simulated sunlight exposed oil films on the surface of pure and sea water

2) Determine photoproducts for simulated sunlight exposed oil films on the surface of pure and sea water

3) Determine the effects of photocatalyst nanoparticles (e.g. TiO$_2$ NP and TiO$_2$ NT) on the rate, products, and mechanisms of oil exposed to simulated sunlight in or on pure water or sea water
CHAPTER 2. INSTRUMENTATION

Solar Simulator

For photochemical studies, an Atlas CPS+ solar simulator was used at an intensity equivalent to approximately 1.26 times that of solar noon (AM 1.5). The optical spectrum of the irradiation source in the solar simulator used in our studies was similar to the optical spectrum of the sun, with a slightly higher intensity. To standardize our instrument, a Hamamatsu S1718 solar cell (calibrated at the National Renewable Energy Laboratory) was used to measure the intensity of light in the simulator. From the measured intensity, it was discovered that the output of our solar simulator set at its maximum output (765 W/cm², 300-800 nm only) was equivalent to 1.26 times the intensity of full sunlight (1000 W/m² full spectrum AM 1.5).

Based on solar irradiance data from the National Solar Radiation Database latitude 28.85, longitude -88.35 (the nearest location to our sampling site), the average daily amount of direct and diffuse solar radiation received on a horizontal surface at this location in 2009 was 4972 Wh/m². Our solar simulator produced about 1260 W/m². Dividing this irradiance into the average daily insolation yields a value of 3.95 h, representing the amount of time in our solar simulator equivalent to an average day of insolation at this location.

Mass Spectrometry

Mass Spectrometry is a technique used to determine the mass to charge (m/z) ratio of a given analyte. The mass to charge ratio is the mass of the ion on the atomic scale divided by the number of charges that the ion possesses. Gas-phase ions of a given analyte are produced and grouped accordingly to their unique properties and positioned in space so they may be manipulated with the use of electric or magnetic fields. This technique can given structural information based on specific features of the analyte such as nominal mass, molar mass and fragmentation patterns. Analyses are typically run under vacuum to free ions from other forms of matter. Mass spectrometers have many types of ion sources, mass analyzers and detectors. **Ion Source.** There are several ionization techniques, which are used to introduce samples into the mass spectrometer. There are sensitive and soft ionization techniques such as electrospray ionization (ESI) or matrix-assisted laser desorption/ionization (MALDI). Atomospheric pressure photoionization (APPI) uses UV photons to ionize the sample. Each ionization
technique targets specific types of analytes and mass ranges. This research thesis will primarily focus on electrospray ionization techniques.

Electrospray Ionization (ESI) creates multiply charged ions in solution through acid-base chemistry. The ions are transferred to the gas phase by passing the analyte solution through a charged needle at atmospheric pressure. A nebulizer gas sprays the charged droplets into a chamber containing drying gas which causes the solvent surrounding the ions to evaporate or desolvate\(^\text{47}\). The desolvation of the solvent decreases the size of the droplet size until the ions begin to repel one another. The repulsion causes a coulombic explosion between the charges until the Rayleigh limit is reached. Individual gas-phase analyte ions are then introduced into the mass analyzer.

![Figure 2.1. Schematic of electrospray ionization.](image)

**Mass Analyzer.** A mass analyzer separates ions according to their mass to charge ratio based on characteristic behavior in electric or magnetic fields. These behaviors are used to separate ions of different \(m/z\) values in space or time allowing for the determination of individual...
abundances. Types of mass analyzers include quadrupole, magnetic sector, ion trap, time-of-flight and Fourier transform ion cyclotron resonance (FT-ICR). Each mass analyzer has different characteristics and sensitivity depending on the application, resolution, or performance desired. This research thesis will focus on FT-ICR mass spectrometry and its use to analyze water soluble organics produced as a result of photodegradation of petroleum.

**Fourier transform ion cyclotron resonance mass spectrometry.** In 1974, Melvin Comisarow and Alan Marshall combined Fourier transforms, ion cyclotron resonance and mass spectrometry to invent FT-ICR mass spectrometry. Since it’s launch it has become a widely used technique. The fundamental principles of FT-ICR MS encompasses ion cyclotron frequency, ion cyclotron motion, and confinement of ions. Mass analysis using FT-ICR MS is performed at high vacuum, 10^{-10} torr. This study utilized this technique due to its high resolution capabilities.

**Data Representation**

In order to visualize trends and differences between samples, data obtained from FT-ICR MS was graphically represented in a variety of different methods. These methods made it possible to distinguish amongst thousands of compounds in a complex mixture such as petroleum or WSO.

**The van Krevelen Diagram.** The van Krevelen diagrams plot the molar H/C ratios on the y-axis and the molar O/C ratios on the x-axis, and are utilized to assist in clustering molecules according to their functional group compositions. The diagram displays one data point for each molecular formula assigned from one resolved peak on the mass spectrum. Figure 2.2 shows an example of a van Krevelen diagram. This diagram enables samples that are processed differently to be distinguished by the location of each point on the plots.
Isoabundance Plots. Isoabundance plots compare double bond equivalency (DBE) vs. carbon number. Figure 2.2 shows an example of an isoabundance plot. DBE is a measure of the hydrogen saturation where a DBE value equal to zero describes a fully saturated molecule. These plots are graphical images which are formed from heteroatoms classes in order to sort thousands of chemical formulas and compare each sample class. These images can illustrate compositional changes between samples such as dark vs. irradiated.

Figure 2.3. Example of van Krevelen diagram. The green dots represent compounds unique to dark and the blue represent compounds unique to irradiated.

Figure 2.4. Shows an example of an isoabundance plot where DBE is representative of number of rings plus double bonds.
Chapter 3. Petroleum Films Exposed to Sunlight Produce Hydroxyl Radical

Abstract

Sunlight exposed oil films on seawater or pure water produced substantial amounts of hydroxyl radical as a result of irradiation. Oil was collected from the surface of the Gulf of Mexico following the Deepwater Horizon spill and exposed to simulated sunlight in thin films over water. Photochemical production of hydroxyl radical was measured with benzoic acid as a selective chemical probe in the aqueous layer. Total hydroxyl radical formation was studied using high benzoic acid concentrations and varying exposure time. The total amount of hydroxyl radical produced in 24 hour irradiations of thin oil films over Gulf of Mexico water and pure water were $3.7 \times 10^{-7}$ and $4.2 \times 10^{-7}$ moles respectively. Steady state concentrations of hydroxyl radical were measured using a competition kinetics approach. Hydroxyl radical concentrations of $1.2 \times 10^{-16}$ to $2.4 \times 10^{-16}$ M were observed for seawater and pure water under oil films. Titanium dioxide (TiO$_2$) nanomaterials were added to the system in an effort to determine if the photocatalyst would enhance oil photodegradation. The addition of TiO$_2$ nanoparticles dramatically changed the observed formation rate of hydroxyl radical in the systems with NP water at pH 3, showing increased formation rate in many cases. With photocatalyst, the steady state concentration of radical decreased, predominantly due to an increase in the hydroxyl radical scavenging rate with oxide present. This study illustrates that
oil is a strong and important source of hydroxyl radical when exposed to sunlight. The fate of oil and other dissolved species following oil spills will be heavily dependent on the formation and fate of hydroxyl radical.

Introduction

Photochemical transformation of intact crude oil has been studied to a limited extent over the last 40 years. In 1975, Hansen reported on the photodegradation of thin films of crude oil fractions on sea water. Photochemical degradation of PAHs in thin films of spilled oil on rocks were investigated. There have been numerous published studies regarding photoproducts produced in natural water from the photolysis of dissolved organic matter (DOM), which consists predominantly of dead plant material. When DOM is exposed to sunlight, a number of reactive transients are formed, including hydroxyl radical, singlet oxygen, superoxide, organic radicals and organic triplets. Methods for quantitating these transients have been reported. Since the composition of DOM varies with its environment, differences in the transients and their functions have been observed. Zhou and Mopper measured the production rates and steady state concentrations of photochemically produced hydroxyl radicals in coastal and open ocean waters and freshwaters. Vaughan and Blough measured OH production rates in the photolysis of fulvic acid solutions in natural water in the presence and absence of dioxygen. There have been many studies done with selective probes to detect the formation of reactive transients. Oil and natural organic matter likely have common origins (dead plant matter) but have different structures and compositions. Despite these differences, they may share similar functional groups and likely have some common mechanisms for photochemical formation of reactive transients. This study focused on the photochemical production of reactive transients that form when sunlight reacts with thin oil films over water. The role of these photochemical transients formed in the presence of thin oil films on water has not been fully explored. Furthermore, the subsequent chemical and biological processes that occur in the aqueous layer when sunlight reacts with oil are poorly understood. In order to better understand these effects when oil is spilled in an aquatic system, the formation and scavenging of hydroxyl radical was studied in oil on water systems under solar irradiation. Hydroxyl radicals have been previously implicated in the degradation of organic pollutants, photo-Fenton chemistry and
the chemistry of natural organic compounds in aqueous environments. Consequently, hydroxyl radical is an important oxidant in the environment. In this study, the total amount of hydroxyl radical formation and the steady state concentrations were determined employing similar methods previously reported by Zhou and Mopper.

This study investigated photochemical formation of hydroxyl radical from crude oil collected from the Deepwater Horizon oil spill that occurred on April 10, 2010. Photochemical production of hydroxyl radical was investigated for oil films on seawater and pure water matrices. Furthermore, this study investigated the effect of photocatalysts on hydroxyl radical formation during solar irradiation. Photocatalysts are a potential method of speeding decomposition of spilled oil, which was our motivation for investigating photocatalyst amended oil. In addition to accelerating overall degradation rates, photocatalysts can change the reaction mechanisms and the products formed. We have evidence that changes in photoproduct identity occurs upon addition of a photocatalyst (See figure A3 in supporting information), although the details are not yet understood. Changes in oil composition and production of photoproducts can exert important influences on oil fate, toxicity, and bioavailability. Changes in toxicity have been observed upon irradiation of oil with simulated sunlight. The fundamental knowledge (hydroxyl radical formation rate, scavenging rate, and steady state concentration) generated by this study may translate into better technologies and better protocols for minimizing the negative impacts of an oil spill in an aquatic system. Titanium dioxide is a low cost, readily abundant, low toxicity material that has potential to enhance oil degradation. Results will help identify low cost, effective remediation strategies in order to better mitigate the harmful effects of an oil spill.

**Experimental**

**Materials**

Pure water was obtained by purification of distilled water with a Barnstead NanopureUV water treatment system (NP water). Gulf of Mexico water (GW) was obtained from the Mississippi Sound and filtered first through 0.45 μm membrane filters then 0.2 μm membrane filters (Gelman Science 90 mm Supor-450 and Supor-200, respectively) and stored in the dark at 4°C. The gulf water had a pH of 7.9 and a salinity of 23 ppt. Surface oil was collected on May 24, 2010 directly from the surface of the Gulf of Mexico (latitude 28.801 and longitude -
89.119) about 50 miles NW of the Deepwater Horizon site. This oil had risen to the surface through 1500 m of Gulf water and remained on the surface prior to collection. Therefore, water soluble and volatile compounds had been removed from the surface oil prior to collection. Samples were stored in the dark at 4°C. Benzoic acid (BA, 99.5%), 4-hydroxybenzoic acid (p-HBA, 99+%), 2-hydroxybenzoic acid (salicylic acid) ACS grade, 99+%, 3-hydroxybenzoic acid (99%), and P25 titanium dioxide (99.5%) 1-propanol (PrOH) (99.9%), 2,4 dinitrophenylhydrazine (DNPH) (70%) were purchased from Aldrich. Stearic acid was obtained from JT Baker. Dimethyl sulfoxide (DMSO) (certified ACS), Acetonitrile (ACN), trifluoroacetic acid (TFA), both HPLC grade, were obtained from Fisher. Propionaldehyde (98%) was purchased from Fluka. All reagents were used as received.

**Instrumentation**

For photochemical studies, an Atlas CPS+ solar simulator was used. Refer to Chapter 2 for a more detailed explanation.

Oil samples were placed in a thin film on seawater or pure water containing benzoic acid and exposed to simulated sunlight. The aqueous phase was collected after each irradiation and samples were analyzed for production of 4-hydroxybenzoic acid in triplicate. Reaction products were quantitated by high performance liquid chromatography (HPLC) using an Agilent 1200 series liquid chromatograph equipped with a DAD detector. Absorbance spectra of the eluent were collected from 200-400 nm. An Agilent Eclipse XDB-C18 column (5 μm particle size, 15 cm in length x 4.6 mm id) was used for all separations. The elution gradient was 0.1% aqueous TFA at pH 2.0 (A) and acetonitrile (B): initially at 20 % B, increased linearly to 30% B over 6 minutes to elute p-HBA. After the compounds of interest were eluted, 100% B was flushed through the column to wash out any residual oil photoproducts. A flow rate of 1.0 mL/min was used, and a 100 μL loop was used for injections. For samples that were at pH 8, 5 mM HCl (aq) was added to bring them to pH 3 prior to injection.

**Irradiation procedure**

Benzoic acid was added directly to the water samples. For the gulf water samples, 10 mM concentrations were prepared and mechanically stirred for two days to dissolve the solid. For pure water, a known amount of benzoic acid was added to boiling water, cooled and diluted to volume with pure water. Solutions were adjusted to pH 3 ± 0.04 using dilute HCl and adjusted
to pH 8 ± 0.04 using dilute NaOH. For each exposure, 100 ± 0.4 mg of surface oil was spread evenly on the surface (~60 μm oil thickness) of 10 mL of the aqueous layer. This step was done by dispersing the oil into a mixture of 2.0 mL pentane and 100 μL toluene, sonicating for 2 seconds, and pouring contents over the aqueous layer. Without this dissolution step, the oil was too viscous to spread evenly over the water layer. Samples were kept in a fume hood for 5 minutes to allow evaporation of the added solvents, and then subsequently transferred to the solar simulator. Because pentane and toluene are volatile and have low water solubility, these compounds evaporate relatively quickly. Triplicate irradiations were performed in jacketed beakers with water circulating at 27.0 °C. A quartz lid was placed over the top of each beaker to reduce evaporation. Samples were exposed to various irradiation times ranging from 3-24 hours. Each exposure included a dark control kept under the same conditions. A blank irradiated control without probe in each type of water matrix and a blank irradiated control without oil were exposed under the same conditions.

In separate experiments, we assessed the effect of O₂. 50 mg of surface oil was placed in the bottom of a quartz tube (~1 cm id, 5 mL total volume) and chilled to increase its viscosity. Argon purged, air-saturated, or oxygen-saturated aqueous benzoic acid (10 mM, pH = 8) was carefully added to the tube to eliminate all headspace. The tubes were inverted so the oil remained at the top, placed in a water bath, and irradiated for 12 h. After exposure, the water was sampled and p-HBA was determined by HPLC.

**Hydroxyl Radical Trapping**

Benzoic acid was prepared at 10 mM in pure water or seawater as a probe for complete hydroxyl radical trapping. Oil was added to the surface of the water and the samples were irradiated. 4-Hydroxybenzoic acid, the major product of benzoic acid-hydroxyl radical reaction, was quantitated as a function of irradiation time. The number of moles of p-HBA formed was measured by HPLC, and moles of hydroxyl radical formed was calculated based on the reported ratio of 1 mol p-HBA formed for every 5.9 moles of HO• trapped.

**Alternate Probe Study**

In separate experiments, 1-propyl alcohol (10 mM, aqueous) was used as an alternative probe to verify the presence of hydroxyl radical. Oil was added to the surface of the water and the samples were irradiated for 12 h as described above. In order to detect the main product of
the 1-propyl alcohol-hydroxyl radical reaction (propionaldehyde, 46% yield) after irradiation, samples were derivatized by adding 5 mM DNPH in DMSO in a 4:1 (v/v) ratio. A dark and an irradiated blank without probe were performed in the same manner. After the 12 h derivatization, products were analyzed on a 1200 Series Agilent HPLC with a DAD detector. Absorbance spectra of the eluent were collected from 200-400 nm. An Agilent Eclipse XDB-C18 column (5 μm particle size, 15 cm in length x 4.6 mm id) was used for all separations. The elution gradient was 50% water (A) and acetonitrile (B) for 2 minutes then increased linearly to 100% B over 14 minutes. A flow rate of 1.0 mL/min was used, absorbance was observed at 360 nm, and the sample injection volume was 50 μL.

**Steady State Determination**

Benzoic acid was prepared at varying concentrations (0.1-5 mM) in pure water or seawater and samples were irradiated for 3 h after oil was placed on the surface. The steady state concentration of hydroxyl radical in the absence of the probe ([HO]_{ss}) was determined using the method of Zhou and Mopper. In addition, hydroxyl radical formation (F_{HO}) and scavenging rates (k_s) were also determined.

**Photocatalysts**

Titanium dioxide was selected for use as a photocatalyst to enhance degradation of oil. TiO₂ particles (P25, Aldrich) and nanotubes were used in this study. TiO₂ nanotubes were fabricated in house following the method of Ratanatawanate with minor modifications as described in Appendix A Figure A3. TiO₂ nanotubes were used because of their high surface area and low density (the hollow core contains 90% of the tube volume). We have successfully synthesized TiO₂ nanotubes with 10 nm outer diameters and 2-20 μm lengths using a previously published hydrothermal approach. The nanomaterials were functionalized to improve their mixing with the oil. This step was accomplished by soaking the nanomaterials in an ethanol solution of stearic acid using 0.3 mM, and 0.9 mM concentrations of stearic acid for the 3 mg and 9 mg TiO₂ preparations respectively. After soaking, the particles were washed with ethanol and toluene and then stored in toluene at 4°C protected from light until use. In order to prepare oil films with the modified TiO₂, 3 mg or 9 mg of nanoparticles or nanotubes were suspended in 120 μL of toluene. The toluene suspension of TiO₂ was added to the oil
sample along with pentane as described above. These samples were then irradiated using the same procedure as described above.

**Results and Discussion**

Changes in the chemical composition and optical properties of oil films on water have been reported separately \(^4\). At short solar wavelengths (< 350 nm), 73-99% of the radiation was absorbed within the 60 \(\mu\)m oil film. At 300 nm, 50% attenuation of the radiation was reached in the first 10 \(\mu\)m of the film, and at 350 nm 50% attenuation was reached at 30 \(\mu\)m into the film. Despite strong absorbance of UV radiation by the oil, there was still available radiation for absorption through most of the film and by the oxide when present. The absorbance of the oil decreased by about 20% after 12 hours of irradiation. In addition, large decreases of fluorescence were observed with approximately 60% of fluorescence lost after 12 hours of irradiation. Previous studies have shown that alkane concentrations did not decrease substantially over the times used in this study due to their very slow photochemical transformation \(^5\). The current study focused on formation of hydroxyl radical during irradiation of oil films on water. Two approaches were used. In the first approach, a large concentration of a known hydroxyl radical trap (benzoate) was used in an effort to capture all radical that was formed in irradiations from 3 to 24 hours (equivalent to 0.75 to 6 days of natural sunlight). In the second approach, low concentrations of probe (benzoate) were used in order to determine the steady state concentration of hydroxyl radical during short-term irradiations (3 hours, equivalent to 0.75 days of natural sunlight).

**Total Hydroxyl Radical Trapping**

The rates of photochemically production of hydroxyl radical generated from thin oil films over aqueous solution were determined. The total amount of hydroxyl radical formed was measured using a high concentration of benzoic acid to ensure all radicals were trapped. Figure 3.1a shows the rate of BA reaction as a function of [BA].

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The plateau in this plot shows the concentration at which all of the radical is effectively trapped by BA. The data in Figure 3.1a are represented as a double reciprocal plot in Figure 3.1b. This linearized plot, discussed in the following paragraph, allows determination of hydroxyl radical steady state concentration, formation rate, and scavenging rate constant.

Benzoic acid reaction with hydroxyl radical has been well studied, showing that major products include \( o \)-, \( m \)-, and \( p \)-hydroxybenzoic acids \(^{16}\). In this study, the formation of \( p \)-HBA was monitored due to its better detection limit. Zhou and Mopper previously reported an average value of \( 5.87 \pm 0.18 \) moles of hydroxyl radical trapped per mole of \( p \)-HBA formed \(^{16}\). This value was used in this study to calculate the total amount of hydroxyl radical trapped based on measured \( p \)-HBA concentrations as a function of irradiation time. Initial studies observed total trapping of hydroxyl radical when 10 mM BA was used. These tests were performed by increasing the benzoic acid concentration until the production rate of \( p \)-HBA did not increase further (see Figures 3.1a and A1) \(^{16}\). These results are similar to results from previous studies \(^{16,28}\) using natural water as the source of photochemically produced hydroxyl radicals. Figure 3.2 shows linear production of \( p \)-HBA as a function of irradiation time, with an eventual decrease in production rate at longer irradiation times.

**Figure 3.1.** a) Kinetics of benzoic acid reaction with hydroxyl radical in Gulf of Mexico water at pH 8 under a 100 mg film of surface oil irradiated 3 hours. b) Double reciprocal plot allowing determination of hydroxyl radical formation and scavenging rates.
These results are consistent with previous studies using natural organic matter, and indicate a stable concentration of hydroxyl radical at early times and an eventual decrease in hydroxyl radical forming precursors as the oil was photodegraded. Table 3.1 shows the results of total hydroxyl radical trapping for irradiated oil on water films.

### Table 3.1

<table>
<thead>
<tr>
<th>Irradiation Time (min)</th>
<th>Moles HO Trapped (× 10⁻⁷)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NP Water pH 3</td>
</tr>
<tr>
<td>180</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>360</td>
<td>2.6 ± 0.6</td>
</tr>
<tr>
<td>720</td>
<td>7.1 ± 0.2</td>
</tr>
<tr>
<td>1440</td>
<td>9.0 ± 1.2</td>
</tr>
</tbody>
</table>

**Figure 3.2.** Plot of moles HO trapped vs. irradiation time for Gulf of Mexico water (pH 8). 120 µL of oil was placed over 10 mL of water and irradiated at 1.2 times solar noon intensity (AM 1.5) in a jacketed beaker maintained at 27°C.
Table 3.1. Moles hydroxyl radical produced by exposure of oil to simulated sunlight as measured by trapping with BA. Values presented are averages of three replicates ± one standard deviation. 120 µL of surface oil was placed over 10 mL of water containing 10 mM BA and irradiated at 1.2 times solar noon intensity (AM 1.5) in a jacketed beaker maintained at 27°C.

Experiments were conducted with the water at pH 3 and pH 8. Seawater is typically near pH 8. The lower pH value was used for comparison since the probe used (BA) is mostly in its protonated form at this pH, while it is essentially 100% ionized at the higher pH value. NP water and GW at pH 3 showed substantially different behavior. The moles of HO• trapped for GW at pH 3 were on average 33% lower than that for NP water. However, at pH 8, the results for GW were on average 16% lower than that for NP water. The second order rate constant for benzoic acid reaction with hydroxyl radical is about $1.80 \times 10^{9}$ M$^{-1}$s$^{-1}$. At pH 8, the reactant is predominantly benzoate, with a second order rate constant around $5.87 \times 10^{9}$ M$^{-1}$s$^{-1}$. The slower $p$-HBA production in the GW compared to NP water at pH 3 could be due to a decrease in efficiency of radical production in the presence of a natural water matrix or could be due to competition with a scavenger for reaction with HO•. Seawater contains a considerable amount of chloride and bromide, each of which can scavenge hydroxyl radical ($k_{Cl} = 3.6 \times 10^{9}$, $k_{Br} = 1.1 \times 10^{10}$) (NIST, 2013) Despite the fact that our data (Figure A1) show complete trapping of hydroxyl radical at 10 mM BA, there is likely a residual scavenging effect from the GW matrix that resulted in the decreased amount of radical trapped compared to NP water.

In additional studies, a photocatalyst (TiO$_2$) was added to the system to measure hydroxyl radical production and scavenging in the presence of the photocatalyst. TiO$_2$ has excellent chemical and physical properties that make it useful for the degradation of pollutants in air and water, as well as in water splitting applications. Two different forms of TiO$_2$ were used: P25 obtained from Aldrich and TiO$_2$ nanotubes (TiO$_2$ NT) which were fabricated in-house using a previously published hydrothermal method. TiO$_2$ nanotubes were chosen due to their structural properties. Due to their greater surface to volume ratio, nanotubular TiO$_2$ structures should provide more efficient transport of photogenerated electrons and holes to the surface, have larger surface area, and have a low overall density due to their hollow structure. The expectation with the nanotubes is that upon addition to the oil, the tubes will fill with oil and remain buoyant in the oil layer, thus enhancing photodegradation. These nanomaterials were separately added to the system at two different loadings, 3 mg TiO$_2$ per 100 mg oil (3%) and 9
mg TiO$_2$ per 100 mg oil (9%). Table 3.2 shows the amount of hydroxyl radical trapped as a function of irradiation time for various water samples with different TiO$_2$ loadings.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Irradiation Time (min)</th>
<th>Moles HO Trapped ($\times 10^{-7}$)</th>
<th>NP Water pH 3</th>
<th>NP Water pH 8</th>
<th>Gulf Water pH 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% TiO$_2$</td>
<td>180</td>
<td>1.4 ± 0.2</td>
<td>0.5 ± 0.1</td>
<td>0.24 ± 0.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>2.7 ± 0.4</td>
<td>1.1 ± 0.2</td>
<td>0.75 ± 0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>720</td>
<td>4.8 ± 1.2</td>
<td>2.3 ± 0.1</td>
<td>2.0 ± 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1440</td>
<td>8.9 ± 1.5</td>
<td>4.1 ± 0.6</td>
<td>2.5 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>9% TiO$_2$</td>
<td>180</td>
<td>2.0 ± 0.5</td>
<td>0.5 ± 0.1</td>
<td>0.41 ± 0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>3.3 ± 0.6</td>
<td>1.5 ± 0.0</td>
<td>1.1 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>720</td>
<td>7.3 ± 1.0</td>
<td>2.4 ± 0.5</td>
<td>2.4 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1440</td>
<td>11.7 ± 3.0</td>
<td>7.0 ± 1.5</td>
<td>3.9 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>3% TiO$_2$, NT</td>
<td>180</td>
<td>0.8 ± 0.1</td>
<td>0.33 ± 0.03</td>
<td>0.17 ± 0.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>1.6 ± 0.3</td>
<td>1.5 ± 0.1</td>
<td>0.46 ± 0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>720</td>
<td>2.3 ± 0.2</td>
<td>1.5 ± 0.1</td>
<td>1.6 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1440</td>
<td>2.5 ± 0.2</td>
<td>2.2 ± 0.1</td>
<td>1.8 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>9% TiO$_2$, NT</td>
<td>180</td>
<td>1.1 ± 0.1</td>
<td>0.29 ± 0.04</td>
<td>0.1 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>1.6 ± 0.1</td>
<td>0.58 ± 0.03</td>
<td>0.53 ± 0.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>720</td>
<td>2.9 ± 0.7</td>
<td>1.2 ± 0.1</td>
<td>1.3 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1440</td>
<td>2.0 ± 0.3</td>
<td>1.4 ± 0.2</td>
<td>1.5 ± 0.4</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2. Moles hydroxyl radical produced by exposure of oil to simulated sunlight as measured by trapping with BA. Values presented are averages of three replicates ± one standard deviation. 120 µL of surface oil containing oxide was placed over 10 mL of water containing 10 mM BA and irradiated at 1.2 times solar noon intensity (AM 1.5) in a jacketed beaker maintained at 27°C.

In the case of NP water at pH 3 (9.0 ± 1.2 moles HO• trapped) compared to NP water with 9% TiO$_2$, NT at pH 3 (2.0 ± 0.3 moles HO• trapped), the presence of oxide had a dramatic impact on the amount of hydroxyl radical trapped. For 3% TiO$_2$ in pure water at pH 3 or 8, the total moles trapped were comparable to that for the no oxide system. However, GW with 3% TiO$_2$ at pH 8 showed a substantially lower amount of radical trapped. For all waters tested (NP at pH 3 and 8; GW at pH 8), addition of 9% TiO$_2$ showed much lower amounts of radical trapped. Furthermore, at both 3% and 9% TiO$_2$, NT for all waters tested, the largest decrease in hydroxyl
radical trapping was observed. These results are contrary to expectations since irradiation of TiO$_2$ is known to produce hydroxyl radical. Addition of a second source of the radical should enhance the radical production rate. However, the oxide was completely within the oil phase, which may have dramatically prevented either the formation of hydroxyl radical or the transport of the radical into the aqueous phase. The commonly accepted pathways for hydroxyl radical formation from TiO$_2$ involve direct oxidation of water by holes or reduction of O$_2$ by electrons followed by further reaction to yield hydroxyl radical. In either case, interaction with water is an essential step in hydroxyl radical formation. Hydroxyl radical or other reactive transients formed at the surface of the oxide may have been rapidly intercepted by nearby oil or by other transients present at high concentration at the particle-oil interface. A high concentration of hydroxyl radicals at the particle surface would enhance hydroxyl radical-hydroxyl radical reaction to form H$_2$O$_2$. The very large effect observed for the nanotubes is likely due to its high surface area, which would contribute to enhanced radical-oil interaction as well as enhanced radical-radical reaction.

**Steady State Determination**

Competition kinetics experiments were conducted using various concentrations of benzoic acid and a constant irradiation time of 3 hours. It is known that hydroxyl radical has a low steady state concentration in natural waters, and it is difficult to measure without the use of a chemical probe. In a classic competition kinetics experiment, the probe is competing with other scavengers in the water samples. These experiments are carried out by measuring the overall HO• reaction rate with an added scavenger at several concentrations. In an application of the approach of Zhou and Mopper, whose work focused on natural organic matter, we examined the role of crude oil as a source of hydroxyl radicals. Hydroxyl radicals are photochemically produced with a formation rate, $F_{HO}$, which is constant under constant solar flux provided that the organic matter is not depleted. Produced hydroxyl radicals react with scavengers (S) present in the sample with a rate $R_s$ and a corresponding second order rate constant, $k_s$. Any added probe scavenger, P, reacts with a rate $R_p$ and a corresponding rate constant, $k_p$. In our study, the oil acted as both the source and scavenger for hydroxyl radicals. Under constant irradiation flux, the system rapidly reaches steady state such that:

$$F_{HO} = R_s + R_p$$  \hspace{1cm} (1)
yielding a steady state concentration of hydroxyl radical, $[\text{HO}]_{\text{ss}}$. Since the steady state concentration for hydroxyl radicals cannot be measured directly, it is measured through the manipulation of a series of equations where $F_{\text{HO}}$, $k'_{s}$ (pseudo first order rate constant), and $[\text{HO}]_{\text{ss}}$ can be calculated for any system using equations 2 and 3:

$$\frac{1}{R_p} = \frac{1}{F_{\text{HO}}} + \frac{k'_{s}}{F_{\text{HO}} k_p} \times \frac{1}{[P]}$$

(2)

$$[\text{HO}]_{\text{ss}} = \left[ \frac{(k'_{s} + k'_{p})}{(k'_{s} \times k'_{p})} \right] \times R_p$$

(3)

Plotting equation 2 as $1/R_p$ vs. $1/[P]$ produces a straight line such that the reciprocal of the y-intercept is $F_{\text{HO}}$, the slope can be used to calculate $k'_{s}$, and equation three yields $[\text{OH}]_{\text{ss}}$ (see Fig. 3.1b).

As reported in the earlier work, a saturation or plateau in $R_p$ was observed as the concentration of benzoic acid increased to a high enough value that essentially all hydroxyl radicals were trapped by the added probe, which outcompeted other scavengers at these high probe concentrations (See Figures 1.3 and A1). Table 3.3 presents the results for $F_{\text{HO}}$, $[\text{HO}]_{\text{ss}}$, and $k_s$ for oil on water films.

<table>
<thead>
<tr>
<th>Water</th>
<th>pH</th>
<th>$F_{\text{HO}}$ ($M \text{s}^{-1} \times 10^{-10}$)</th>
<th>$k'_{s}$ ($s^{-1} \times 10^{5}$)</th>
<th>$[\text{OH}]_{\text{ss}}$ ($M \times 10^{-16}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP</td>
<td>3</td>
<td>9.6</td>
<td>8.4</td>
<td>11.7 ± 0.24</td>
</tr>
<tr>
<td>NP</td>
<td>8</td>
<td>3.6</td>
<td>15.5</td>
<td>2.4 ± 0.33</td>
</tr>
<tr>
<td>GW</td>
<td>3</td>
<td>4.5</td>
<td>12.0</td>
<td>3.6 ± 0.39</td>
</tr>
<tr>
<td>GW</td>
<td>8</td>
<td>4.0</td>
<td>32.0</td>
<td>1.2 ± 0.20</td>
</tr>
</tbody>
</table>

Table 3.3. Formation rate of HO•, pseudo first order rate constant for scavengers in the oil/water system, and steady state concentration of HO• for several oil/water systems. Uncertainty in $F_{\text{HO}}$ and $k'_{s}$ were typically 30%. For $[\text{OH}]_{\text{ss}}$, reported error is one standard deviation for 6 measurements. 120 µL of surface oil was placed over 10 mL of water containing varying concentrations of BA and irradiated for 3 h at 1.2 times solar noon intensity (AM 1.5) in a jacketed beaker maintained at 27°C.

The observed $[\text{OH}]_{\text{ss}}$ was greater in nanopure water than in Gulf water likely due to increased scavenging by chloride, bromide, and other natural scavengers in the Gulf water. The hydroxyl
radical formation rate in pure water and Gulf water at pH 8 were similar. However, the scavenging rate constant at pH 8 in the Gulf water was more than double that in pure water. This observation is in agreement with the lower observed [OH]_s, and the fact that natural scavengers are present in the Gulf water. Measurements made at pH 3 showed 3-5 times larger hydroxyl radical [OH]_s than measurements made at pH 8. At the same time, a lower scavenging rate constant was observed at low pH, suggesting that the scavenging processes are inhibited at pH 3. Comparing to the values observed by Zhou and Mopper for irradiated pure seawater samples, our results show 10-30 times greater hydroxyl radical formation rates and 10-40 times higher [OH]_s. Consequently, seawater near the oil film would have substantially enhanced hydroxyl radical concentrations compared to uncontaminated seawater. Open ocean waters have very low concentrations of DOM, so oil at the surface of these waters will predominate the production of hydroxyl radical. In coastal regions where DOM concentrations are higher, the DOM will have a much greater impact on radical scavenging as well as radical formation. Any light penetrating through the oil layer can interact with DOM to cause photochemical formation of hydroxyl radical as previously reported 51. However, optically thick oil films will prevent DOM photochemistry by absorbing all available light.

To test the ability of TiO$_2$ to speed oil decomposition through photocatalysis, additional studies were performed with added TiO$_2$, and the results are presented in Table 3.4.
Table 3.4. Formation rate of HO•, pseudo first order rate constant for scavengers in the oil/water system, and steady state concentration of HO• for several oil/water systems. Uncertainty in $F_{\text{HO}}$ and $k_s'$ were typically 30%. For $[\text{OH}]_{\text{SS}}$, reported error is one standard deviation for 3 to 6 measurements.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Water</th>
<th>pH</th>
<th>$F_{\text{HO}}$ (M s$^{-1} \times 10^{10}$)</th>
<th>$k_s'$ (s$^{-1} \times 10^5$)</th>
<th>$[\text{OH}]_{\text{SS}}$ (M $\times 10^{16}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% TiO$_2$</td>
<td>NP</td>
<td>3</td>
<td>7.2</td>
<td>23.7</td>
<td>3.1 ± 1.0</td>
</tr>
<tr>
<td>9% TiO$_2$</td>
<td>NP</td>
<td>3</td>
<td>8.0</td>
<td>26.3</td>
<td>1.7 ± 0.70</td>
</tr>
<tr>
<td>3% TiO$_2$ NT</td>
<td>NP</td>
<td>3</td>
<td>12.0</td>
<td>132.4</td>
<td>1.2 ± 0.54</td>
</tr>
<tr>
<td>9% TiO$_2$ NT</td>
<td>NP</td>
<td>3</td>
<td>36.5</td>
<td>345.8</td>
<td>1.1 ± 0.22</td>
</tr>
<tr>
<td>3% TiO$_2$</td>
<td>GW</td>
<td>8</td>
<td>3.2</td>
<td>226.0</td>
<td>0.15 ± 0.02</td>
</tr>
<tr>
<td>9% TiO$_2$</td>
<td>GW</td>
<td>8</td>
<td>3.2</td>
<td>1350.0</td>
<td>0.26 ± 0.06</td>
</tr>
<tr>
<td>3% TiO$_2$ NT</td>
<td>GW</td>
<td>8</td>
<td>5.8</td>
<td>1160.0</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>9% TiO$_2$ NT</td>
<td>GW</td>
<td>8</td>
<td>5.0</td>
<td>1370.0</td>
<td>0.037 ± 0.002</td>
</tr>
<tr>
<td>3% TiO$_2$</td>
<td>NP</td>
<td>8</td>
<td>4.7</td>
<td>141.0</td>
<td>0.34 ± 0.03</td>
</tr>
<tr>
<td>9% TiO$_2$</td>
<td>NP</td>
<td>8</td>
<td>3.5</td>
<td>50.3</td>
<td>0.7 ± 0.2</td>
</tr>
<tr>
<td>3% TiO$_2$ NT</td>
<td>NP</td>
<td>8</td>
<td>2.2</td>
<td>147.0</td>
<td>0.16 ± 0.04</td>
</tr>
<tr>
<td>9% TiO$_2$ NT</td>
<td>NP</td>
<td>8</td>
<td>3.0</td>
<td>319.0</td>
<td>0.099 ± 0.020</td>
</tr>
</tbody>
</table>

Overall, the systems with added oxide exhibited dramatically lower steady state concentration of hydroxyl radical as compared to systems with no oxide. These lower values were attributed to very large scavenging rate constants observed in the presence of the oxide. Although added oxide showed enhanced hydroxyl radical formation rates in some cases, the very large scavenging rates resulted in a depressed steady state concentration detected in the aqueous layer. Upon absorption of a photon, a hole-electron pair is created in the oxide. After diffusion to the surface, the electron or hole can result in hydroxyl radical formation in the presence of water or oxygen. Rapid trapping of formed radicals can occur through reaction with oil components, which were in close proximity to the radical formation site since the particles were suspended in the oil layer. In addition, high concentrations of hydroxyl radical formed at or near the particles would be likely to react with each other to form hydrogen.
peroxide. This self-scavenging process could be responsible for the large observed pseudo first order scavenging rate constants. In all cases, the nanotubes resulted in larger scavenging rate constants compared to the nanoparticles. Consequently, the nanotube systems showed lower steady state hydroxyl radical concentrations. These differences were often dramatic. Because the nanotubes have a greater surface area to volume ratio, they were more likely to participate in surface controlled processes that resulted in effective scavenging. In a separate study, we observed that nanoparticles generally enhanced the rate of photochemical degradation of polycyclic aromatic hydrocarbons (PAHs) in oil on water films. Furthermore, nanotubes were even more effective at bringing about PAH photodegradation. These results support the conclusion that oil molecules are effective at rapidly scavenging radicals formed at the surface of the nanoparticles. Addition of TiO$_2$ nanoparticles or nanotubes enhanced loss of PAHs in the oil phase but also resulted in lower concentrations of hydroxyl radical in the aqueous layer under the oil film. Consequently, the effects of photocatalysts on photochemistry of oil on water films will likely be most important in the oil film itself.

### Role of Oxygen

In order to assess the role of oxygen in the formation of hydroxyl radical experiments were performed with altered oxygen content. A 12 h irradiation of 50 mg of oil in 5 mL of oxygen saturated NP water at pH 8 yielded about twice the amount of hydroxyl radical ($2.1 \times 10^{-7}$ moles) compared to a system that was air equilibrated ($1.0 \times 10^{-7}$ moles). Based on the results in this study, the enhancement of hydroxyl radical formation in the presence of elevated oxygen content strongly suggests that oxygen plays an important role in the formation of hydroxyl radical. In an argon purged system, significantly less hydroxyl radical was produced ($0.59 \times 10^{-7}$ moles) compared to the air equilibrated system, providing additional evidence that oxygen is involved in the formation of hydroxyl radical. Residual oxygen after argon purging is most likely the reason why we did not see complete inhibition of hydroxyl radical formation. Several likely pathways for hydroxyl radical formation from irradiation of PAHs are illustrated in Figure 3.3.
All of these pathways involve oxygen and subsequent formation of superoxide. Hydroxyl radical has been shown to be formed through further reaction of superoxide as also shown in Scheme 1. Blough et al. proposed similar pathways for PAH photochemistry\(^\text{64}\), indicating the importance of oxygen. Although other pathways of hydroxyl radical formation are not precluded, the pathways presented here and by Blough et al are the most likely mechanisms for hydroxyl radical formation from irradiation of oil.

**PrOH as an Alternative Probe**

In order to confirm that benzoic acid was in fact reacting with hydroxyl radical, an alternative probe was used. PrOH has a known reaction rate constant of \(2.8 \times 10^9\) M\(^{-1}\)s\(^{-1}\) with hydroxyl radical\(^\text{65}\). This reaction yields 46% propionaldehyde\(^\text{65}\). After a 12 h irradiation of

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**Figure 3.3.** Scheme representing photochemical formation of hydroxyl radical.
oil on water containing PrOH, propionaldehyde was observed by derivatization with DNPH followed by HPLC analysis. The presence of propionaldehyde in the irradiated samples confirmed that thin oil films did produce hydroxyl radical. Dark controls revealed only a trace of propionaldehyde as an impurity in the PrOH.

**Conclusion**

Solar irradiated petroleum films on water represent a very large source of hydroxyl radical. These radicals will play a major role in both degradation of oil compounds as well as the oxidation of other materials present (e.g. dissolved or particulate natural organic matter, dissolved inorganic matter, and microorganisms). Despite the large formation of hydroxyl radical, there are barriers to transport of these radicals into the aqueous layer, including scavenging by oil compounds or self reaction to produce peroxide. TiO$_2$ nanomaterials added to the oil layer, which could be used to speed degradation of oil after spills, dramatically enhanced the formation of hydroxyl radical in the oil film. However, a corresponding enhancement in scavenging resulted in decreased observed aqueous concentration of hydroxyl radical in the presence of the oxide. Based on the cost of TiO$_2$, application at 1% by weight would be cost competitive with the use of commercial dispersants for mitigation of oil spills.
CHAPTER 4. Solar Production of Singlet Oxygen from Crude Oil Films on Water

Abstract

Photochemical production of singlet oxygen from thin oil films over seawater and pure water was measured with furfuryl alcohol as a selective chemical probe. Oil was collected from the surface of the Gulf of Mexico following the Deepwater Horizon spill and from other sources. The loss of furfuryl alcohol and the formation of 6-hydroxy(2H)pyran-3(6H)-one were monitored. Total singlet oxygen formation was studied using high furfuryl alcohol concentrations and varying exposure time. The total amount of singlet oxygen produced in 1 hour irradiations of thin oil films (100 mg, 60 microns thick) over Gulf of Mexico water and pure water were $1.9 \pm 0.4 \times 10^{-5}$ and $1.6 \pm 0.3 \times 10^{-5}$ mol, respectively. After initial tests were performed, titanium dioxide (TiO$_2$) nanomaterials were added to the system in two different concentrations to study the effects of singlet oxygen formation in the presence of a photocatalyst. The addition of TiO$_2$ nanoparticles did not significantly change the observed formation rate of singlet oxygen. Steady state concentrations of photoproduced singlet oxygen were also determined and found to be near $1 \times 10^{-12}$ M in water under thin films of oil, which is considerably greater than values previously observed for pure seawater. This study illustrates
that oil is a source of singlet oxygen when exposed to sunlight. The fate of oil and other
dissolved species will be heavily dependent on the formation and reaction of singlet oxygen in
thin oil films on water.

Introduction

Extensive research has been performed on the photochemistry of natural organic matter
in aquatic systems. Dissolved organic matter (DOM) consists of a group of natural compounds
composed of humic substances, which are typically derived from dead plants and organisms
found in their surrounding environment \(^{15}\). These compounds can generate reactive species
through the acceptance of solar energy. They can produce a number of different types of
reactive species including hydroxyl radical \(^{16,29,30,66,67}\), superoxide \(^{19}\), organic radicals \(^{20-22}\),
organic triplets \(^1\), and singlet oxygen \(^{18,32,33,68-71}\). Singlet oxygen (\(^1\)O\(_2\)) is generated from the
excitation of ground state triplet oxygen, generally through energy transfer from another
excited species. The process occurs when light promotes a chromophore to its first excited
state and then a change in the spin state occurs to the lowest triplet state \(^{33}\). When the triplet
state transfers energy to ground state oxygen, singlet oxygen is produced. According to
Changtong et al, the lifetime of singlet oxygen is short, in the range of 10\(^{-6}\)-10\(^{-2}\) seconds \(^{33}\).
Due to this short lifetime, singlet oxygen is difficult to measure directly. The use of a chemical
probe or scavenger allows relatively easy determination of its steady state concentration.
Many scavenger studies have been reported for singlet oxygen. A kinetic model described by
Haag and Hoigné determined the amount of singlet oxygen produced in water from sunlight
irradiated dissolved organic matter using furfuryl alcohol (FFA) as a chemical probe \(^{32}\). The
current study utilized the methodologies and kinetic model developed by Haag and Hoigné to
determine the production of singlet oxygen from thin crude oil films using FFA as a trapping
agent \(^{18,32}\). In the current study, the model for DOM production of singlet oxygen was applied
to the oil system due to the fact that crude oil also originates from dead plant matter and
contains some similarities in chromophores. However, the chemical structures of crude oil are
substantially different from those found in DOM. A major class of molecules that is involved
in oil photochemistry consists of polycyclic aromatic hydrocarbons (PAHs) \(^3\). Despite the
differences in the source, the role of singlet oxygen in the environment does not change. Crude
oil can participate in many photochemical processes similar to that of DOM that result in the
formation of reactive transients \(^{27}\). Singlet oxygen can produce oxidative transformations of organic pollutants such as phenolic, heterocyclic and olefinic compounds \(^{34,35}\). Haag and Hoigné performed another study focusing on photochemical formation and steady state concentration determination of \(^{1}O_2\) in natural waters \(^{18}\). That study demonstrated the pathway after DOM absorbs a photon and transfers the energy to dissolved oxygen \(^{18}\). Tratnyek et al studied \(^{1}O_2\) kinetics in a solution of 2,4,6 trimethylphenol (TMP) and observed its behavior in seawater systems containing solar production of \(^{1}O_2\) \(^{68}\). Their work led to further understanding of the photooxidation pathways which affect phenols in natural waters \(^{68}\). Other work has been published focusing on the generation of singlet oxygen from petroleum and its fractions \(^{71}\). Correa et al measured the quantum yields of \(^{1}O_2\) and found that the polar and aromatic fractions had the highest quantum yields for \(^{1}O_2\) generation \(^{71}\). The Corrêa study demonstrated that the formation of \(^{1}O_2\) is a general process when petroleum and its fractions are exposed to sunlight \(^{71}\). Other studies have reported that organic compounds that have many rings are capable of reversibly trapping and storing singlet oxygen \(^{33}\). Since the composition of oil is made up of many aromatic compounds, \(^{72-74}\), we expect a large generation of singlet oxygen as a result of solar exposure of oil. Similar to Correa et al, this study demonstrated the formation processes of \(^{1}O_2\) \(^{71}\). Furthermore, the generation of \(^{1}O_2\) was quantified by observing the total amount of \(^{1}O_2\) produced as a function of irradiation time, and the steady state concentration of \(^{1}O_2\) produced in water under thin oil films was determined. Additionally, titanium dioxide (TiO\(_2\)) nanomaterial, a known photocatalyst, was added to the oil. The motivation behind the use of TiO\(_2\) was to create a potential method of speeding decomposition of spilled oil. Previous studies have shown that the addition of a photocatalyst enhances the degradation of PAHs in irradiated thin oil films over water \(^{4}\). This paper studied the impact of photocatalysts on singlet oxygen formation and steady state concentration.

The primary motivation for this work was to understand the basic mechanisms and processes that occur when sunlight interacts with oil after an oil spill has occurred. Elucidating the mechanisms and pathways of photolytic and photocatalytic oil degradation using scavenger studies is important to understand the fate of the oil after it is exposed to sunlight. The oil used in this study included samples collected from the Deepwater Horizon (DWH) spill, which occurred on April 10, 2010. This study will enhance fundamental knowledge regarding the pathways and mechanisms of oil degradation. This knowledge can then be used to help to
predict oil behavior and to develop improved remediation efforts for future oil spills.

**Materials and Methods**

**Materials**

Pure water was obtained by purification of distilled, deionized water with a Barnstead NanopureUV water treatment system (NP water). Gulf of Mexico water (GW) was obtained from the Mississippi Sound and filtered first through a 0.45 μm membrane filter then a 0.2 μm membrane filter (Gelman Science 90 mm Supor-450 and Supor-200 respectively) and stored in the dark at 4°C. The Gulf water had a pH of 7.9 and a salinity of 23 ppt. Weathered DWH oil (surface oil) was collected on May 24, 2010 directly from the surface of the Gulf of Mexico (48.316 N, 89 07.949 W) about 50 miles NW of the Deepwater Horizon site. This oil had risen to the surface through 1500 m of Gulf water and remained on the surface prior to collection. Therefore, volatile compounds and compounds with even modest water solubility had been removed from the weathered DWH oil prior to collection. Oil samples were stored in the dark at 4°C. Additional oil samples included four samples obtained from NIST: SRM 8505 or VAN (V in crude oil), SRM 2171a or HFO #1 (S in residual fuel oil 3%), SRM 1622e or HFO #2 (S in residual fuel oil 2%), and SRM 1620e or HFO #3 (S in residual fuel oil 4%). DWH crude oil from the Macondo well (MC 252) was received from BP (August 2011, chain of custody number 20110803-Tarr-072). Furfuryl alcohol (98%) and 6-hydroxy(2H)pyran-3(6H)-one (6-HP-one, 95%) were purchased from Sigma Aldrich. Rose Bengal, methanol, and titanium dioxide (99.5% P25) were purchased from Aldrich. Stearic acid powder was obtained from JT Baker. Acetonitrile (ACN), HPLC grade, was obtained from EMD. All reagents were used as received.

**Sample Preparation**

Oil samples were placed in a thin film on seawater or NP water containing furfuryl alcohol and exposed to simulated sunlight in triplicate. The aqueous phase was collected after each irradiation and samples were analyzed for loss of FFA and formation of 6-hydroxy(2H)pyran-3(6H)-one.
Instrumentation

For photochemical studies, an Atlas CPS+ solar simulator was used (refer to chapter 2 for a detailed description regarding the simulator).

Reaction products were quantitated by high performance liquid chromatography (HPLC) using an Agilent 1200 series liquid chromatograph equipped with a diode array absorbance detector. Absorbance spectra of the eluent were collected from 200-400 nm and quantitation was performed using absorbance at 219 nm. An Agilent Eclipse XDB-C18 column (5 µm particle size, 15 cm in length x 4.6 mm id) was used for all separations. The elution was isocratic at 90% water and 10% acetonitrile for 5 minutes. Then 100% acetonitrile was eluted over 7 minutes to wash out any residual oil photoproducts. A flow rate of 1.0 mL/min was used, and a 100 µL loop was used for injections.

Irradiation procedure

Furfuryl alcohol was added directly to the water samples before irradiation. For each exposure, 100 ± 0.4 mg of weathered DWH oil was spread evenly (~60 µm oil thickness) on the surface of 10 mL of the aqueous layer. This step was done by dispersing the oil into a mixture of 2.0 mL pentane and 100 µL toluene, sonicating for 2 seconds, and pouring contents over the aqueous layer. Without this dissolution step, the oil was too viscous to spread evenly over the water layer. Samples were kept in a fume hood for 5 minutes to allow evaporation of the added solvents, and then subsequently transferred to the solar simulator. Because pentane and toluene are volatile and have low water solubility, these compounds evaporate relatively quickly and were not observed in later analysis of the samples. Triplicate irradiations were performed in jacketed beakers with water circulating at 27.0 °C. A quartz lid was placed over the top of each beaker to reduce evaporation. Samples were exposed to various irradiation times ranging from 15 minutes to 1 hour. Each exposure included a dark control kept under the same conditions. A blank irradiated control without probe in each type of water matrix and a blank irradiated control without oil were exposed under the same conditions. Selective quenching studies were performed with methanol and rose Bengal to determine the involvement of hydroxyl radical. These studies were done under aerated conditions. A 20 µM solution of rose Bengal, a known singlet oxygen sensitizer, was added with and without oil to monitor the loss of FFA and the generation of 6-HP-one. A second study was performed with
methanol, \( k = 8.3 \times 10^8 \text{M}^{-1}\text{s}^{-1} \) for reaction with singlet oxygen\(^{(7575757575757575)} \) (NIST.com) to observe any changes in the rate of loss of FFA with the hydroxyl radical scavenger (methanol) present. Methanol was added in 1:1, 1:15 and 1:150 ratio to 0.01 M FFA with 20 µM rose Bengal. One hour irradiations were performed with and without oil.

**Total Singlet Oxygen Trapping**

Furfuryl alcohol was prepared at 0.01 M in pure water or seawater as a probe for total singlet oxygen trapping. Oil was added to the surface of the water and the samples were irradiated. The major product of singlet oxygen reaction with furfuryl alcohol, (6-HP-one), was quantitated as a function of irradiation time using HPLC.

**Steady State Determination**

Furfuryl alcohol was prepared at varying concentrations (2.5 \( \times 10^{-6} \) M to 0.01 M) in pure water or seawater, and samples were irradiated for 30 minutes after oil was placed on the surface. The steady state concentration of FFA in the absence of the probe ([\( ^1\text{O}_2 \)]\(_{ss} \)) was determined using the method of Zhou and Mopper and Haag and Hoigne\(^{16,18,32} \). In addition, singlet oxygen formation (\( F^{1\text{O}_2} \)) and scavenging rate constant (\( k_s \)) were also determined\(^{16} \).

**Photocatalysts**

Titanium dioxide was selected for use as a photocatalyst to enhance degradation of oil. TiO\(_2\) particles (P25, Aldrich) and nanotubes were used in this study. TiO\(_2\) nanotubes were fabricated in house following the method of Ratanatawanate with minor modifications (see Appendix Figure A3)\(^{58} \). TiO\(_2\) nanotubes were used because of their high surface area and low density (the hollow core contains 90% of the tube volume). We have successfully synthesized TiO\(_2\) nanotubes with 10 nm outer diameters and 2-20 µm lengths using a previously published hydrothermal approach (Figure A3)\(^{58} \). The nanomaterials were functionalized to improve their mixing with the oil by soaking in 0.3 mM and 0.9 mM concentrations of stearic acid in ethanol for 3 mg or 9 mg of TiO\(_2\), respectively. Solutions were washed and then stored in toluene at 4°C protected from light until use. In order to prepare oil films with TiO\(_2\), 3 mg or 9 mg of
nanoparticles or nanotubes were suspended in 120 µL of toluene. The toluene suspension of TiO$_2$ was added to the oil sample along with pentane as described above. These samples were then irradiated using the same procedure as described above.

**Results and Discussion**

Changes in the chemical composition and optical properties of oil films on water have been reported separately $^4, 57$. At short solar wavelengths ($< 350$ nm), $> 99\%$ of the radiation was absorbed within the 60 µm oil film for all oils studied. The optical properties of the oils are presented in Table 4.1.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Path Length Required for 90% Attenuation at 350 nm (µm)</th>
<th>$a_{300}$ (cm$^{-1}$)</th>
<th>$a_{350}$ (cm$^{-1}$)</th>
<th>$a_{400}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WDWH</td>
<td>5.7</td>
<td>5531</td>
<td>1757</td>
<td>742</td>
</tr>
<tr>
<td>DWH</td>
<td>9.0</td>
<td>3958</td>
<td>1115</td>
<td>456</td>
</tr>
<tr>
<td>VAN</td>
<td>1.7</td>
<td>13170</td>
<td>5922</td>
<td>3175</td>
</tr>
<tr>
<td>HFO #1</td>
<td>1.2</td>
<td>18070</td>
<td>8406</td>
<td>4325</td>
</tr>
<tr>
<td>HFO #2</td>
<td>1.0</td>
<td>21690</td>
<td>9849</td>
<td>5053</td>
</tr>
<tr>
<td>HFO #3</td>
<td>1.0</td>
<td>20415</td>
<td>10408</td>
<td>5362</td>
</tr>
</tbody>
</table>

**Table 4.1.** Optical properties of oil samples.

For all of the oils used in this study, 90% of the 350 nm radiation was absorbed in the first 1-10 µm of the oil film. Figure 4.1 provides a graphical representation of the optical properties for each oil showing fraction of light absorbed at 350 nm vs. path length within the oil film.
A previous study with weathered DWH oil observed that the absorbance of the oil decreased by about 20% after 12 hours of irradiation and that large decreases of fluorescence were observed with approximately 60% of fluorescence lost after 12 hours of irradiation\textsuperscript{57}. No significant changes in alkane composition were observed on the time scale of that study\textsuperscript{57}. The current study focused on formation of singlet oxygen during irradiation of oil films on water. Two approaches were used. In the first approach, a large concentration of a known singlet oxygen trap (FFA) was used in an effort to capture all transient that was formed in irradiations from 15 to 60 minutes. In the second approach, low concentrations of probe (FFA) were used in order to determine the aqueous steady state concentration of singlet oxygen during short-term irradiations (30 minutes, equivalent to \(~0.13 \) days of natural sunlight).

**Role of Hydroxyl Radical**

\textbf{Figure 4.1.} Fraction of light absorbed at 350 nm vs. path length for each oil
Initial tests were made to determine if hydroxyl radical played a role in the oil system with furfuryl alcohol as the probe. Hydroxyl radical has been previously observed in solar irradiated oil, and consequently we tested if that radical would substantially degrade the FFA. Methanol was added as a singlet oxygen scavenger to systems with rose Bengal or oil as the singlet oxygen source to observe any changes. Under these conditions, addition of methanol did not affect the behavior of FFA as a singlet oxygen trap, indicating that methanol had little effect on the overall FFA consumption. With methanol present, any OH radical should have been effectively scavenged and any reaction of hydroxyl radical with FFA would have been eliminated. The FFA behavior did not change upon the addition of methanol, indicating that OH radical was not a major contributor to FFA loss. This result was also found to be true in other studies using 2-propanol, another known hydroxyl radical scavenger ($k = 1.9 \times 10^9 \text{M}^{-1}\text{s}^{-1}$) \cite{76,77}.

**Total Singlet Oxygen Trapping**

The rates of photochemical production of singlet oxygen generated from thin oil films over aqueous solution were determined. Typically, the total amount of singlet oxygen formed was measured using a high concentration of FFA to ensure all singlet oxygen was trapped. Figure 4.3 shows a plot of FFA reaction rate vs. [FFA] during irradiation of oil on Gulf water.
This plot was used to determine the probe concentration at which nearly all singlet oxygen was trapped by the added FFA. At high concentration of FFA (0.01 M), this plot became flat, indicating that effectively all of the singlet oxygen was trapped. In this study, the formation of 6-HP-one and the loss of FFA were both monitored. The major products of FFA reaction with singlet oxygen have been reported, and 6-HP-one was shown to be formed as the most abundant product. The reactions leading to the production of 6-HP-one and products have been well documented.

Zhou and Mopper previously reported a method to obtain the average value of moles of hydroxyl radical trapped per mole of p-HBA formed. This approach was applied to the FFA/\(^{1}\)O\(_{2}\) system in the current study to determine the average number of moles of 6-HP-one formed per mole of singlet oxygen trapped. The measured values (0.62 ± 0.07 for GW and 0.45 ± 0.04 for NP) were then used to calculate the total amount of singlet oxygen trapped based on measured 6-HP-one concentrations as a function of irradiation time. Studies to measure total singlet oxygen production were performed using 0.01 M FFA, which was determined from Figure 3.3 to be sufficient to effectively trap all of the formed \(^{1}\)O\(_{2}\). Figure 3.4
shows a plot of moles $^1$O$_2$ trapped vs. irradiation time for a weathered DWH oil film on Gulf of Mexico water.

![Plot of moles $^1$O$_2$ trapped vs. irradiation time for Gulf of Mexico water.](image)

**Figure 4.4.** Plot of moles $^1$O$_2$ trapped vs. irradiation time for Gulf of Mexico water. 100 mg of oil was placed over 10 mL of water and irradiated at 1.3 times solar noon intensity (AM 1.5) in a jacketed beaker maintained at 27°C.

After 60 minutes, a plateau or flattening of the curve was observed. The flattening is representative of the depletion of the chromophores in the oil that were producing singlet oxygen. It is therefore apparent that depletion of the source of singlet oxygen compounds occurred on time frames of an hour (equivalent to ~0.25 day of natural sunlight exposure).

The results reported in this paper are similar to results from previous studies using natural water as the source of photochemically produced singlet oxygen$^{18,32}$. However in our case we demonstrated the production of singlet oxygen from thin petroleum films on Gulf water and NP water. The fact that singlet oxygen was produced in NP water systems proves that the compounds in the oil were producing singlet oxygen upon irradiation. Seawater samples with no oil showed minimal $^1$O$_2$ production on the time frame of these experiments, further supporting the conclusion that the oil was the predominant source of singlet oxygen. Table 4.2 shows the results of total moles of singlet oxygen trapped for irradiated oil on water.
films. We observed a substantially higher production of 6-HP-one in the GW compared to NP water; however, no reasonable explanation is readily available.

In subsequent studies, a photocatalyst (TiO$_2$) was added to the system to measure singlet oxygen production and scavenging in the presence of the photocatalyst. TiO$_2$ has excellent chemical and physical properties that make it useful for the photocatalytic degradation of pollutants in air and water, as well as in water splitting applications$^{39,60}$. Two different forms of TiO$_2$ were used: P25 obtained from Aldrich and TiO$_2$ nanotubes (TiO$_2$ NT) which were fabricated in-house using a previously published hydrothermal method$^{58}$. TiO$_2$ nanotubes were chosen due to their structural properties. Nanotubular TiO$_2$ structures can provide faster electron and hole transport capabilities$^{61,78}$, have larger surface area, and have low overall density due to their hollow structure. The expectation with the nanotubes is that upon addition to the oil, the tubes will fill with oil and remain buoyant in the oil layer, thus enhancing photodegradation. These nanomaterials were separately added to the weathered DWH oil system at two different loadings, 3 mg TiO$_2$ per 100 mg oil (3%) and 9 mg TiO$_2$ per 100 mg oil (9%). Table 4.2 shows the moles of singlet oxygen trapped as a function of

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Time (min)</th>
<th>moles $^{1}$O$_2$ Trapped (x 10$^{-6}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No Oxide</td>
<td>3% TiO$_2$</td>
</tr>
<tr>
<td>NP</td>
<td>15</td>
<td>5 $\pm$ 2</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>10 $\pm$ 3</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>14 $\pm$ 4</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>16 $\pm$ 3</td>
</tr>
<tr>
<td>GW</td>
<td>15</td>
<td>7 $\pm$ 2</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>13 $\pm$ 1</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>16 $\pm$ 2</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>19 $\pm$ 4</td>
</tr>
</tbody>
</table>

**Table 4.2.** Moles singlet oxygen produced by exposure of weathered DWH oil to simulated sunlight as measured by trapping with FFA. 100 mg of surface oil was placed over 10 mL of water containing 10 mM FFA and irradiated at 1.3 times solar noon intensity (AM 1.5) in a jacketed beaker maintained at 27°C. Reported error is one standard deviation for N = 3.
irradiation time for various water samples with different TiO$_2$ loadings.
The presence of oxide did not show a dramatic impact on the moles of singlet oxygen trapped as compared to systems with no oxide. This observation was true for both the NP water and the GW systems. This result was expected since TiO$_2$ was found to be unimportant in affecting singlet oxygen produced by rose Bengal$^{68}$. The fact that TiO$_2$ does not interfere with $^1$O$_2$ is important since addition of the TiO$_2$ can enhance other reaction pathways (e.g. hydroxyl radical) without inhibiting singlet oxygen pathways for pollutant degradation.

**Steady State Determination**

Steady state concentration of singlet oxygen in the water layer was determined using two different models. The first model (ZM) followed the work of Zhou and Mopper as previously applied to hydroxyl radical$^{16}$. Following this model, competition kinetics experiments were conducted using various concentrations of FFA and a constant irradiation time of 30 minutes to examine the role of crude oil as a source of singlet oxygen. It is known that singlet oxygen has a low steady state concentration in natural waters, and it is difficult to measure without the use of a chemical probe$^{32,34}$. In a classic competition kinetics experiment, the probe competes with other scavengers in the water samples$^{16}$. These experiments were carried out by measuring the overall $^1$O$_2$ reaction rate with an added scavenger at varying scavenger concentrations$^{16,18,32}$. Figure 4.5a shows the kinetic plot of rate of 6HP-one formation vs. [FFA]. The kinetic plots are consistent with previous studies using natural organic matter$^{16}$ and indicate a decrease in steady state concentration as more probe is added. Figure 4.5b shows an inverse plot of rate of 6HP-one vs. 1/[FFA]; such a plot allows determination of singlet oxygen behavior.
In a typical competition kinetics system, singlet oxygen is photochemically produced with a formation rate, $F_{1O_2}$, which is constant under constant solar flux provided that the source (e.g. petroleum) is not depleted. Produced singlet oxygen reacts with scavengers (S) present in the sample with a rate $R_S$ and a corresponding pseudo first order rate constant $k_S'$. Any added probe scavenger, $P$, reacts with a rate $R_P$ and a corresponding second order rate constant $k_P^{16}$. In our study, the oil acted as both the source and scavenger for singlet oxygen. Under constant irradiation flux, the system rapidly reaches steady state such that:

$$F_{1O_2} = R_S + R_P$$  \(1\)

yielding a steady state concentration of singlet oxygen, $[^1O_2]_{SS}$. Since the steady state concentration for singlet oxygen cannot be measured directly, it is measured through the manipulation of a series of equations where $F_{1O_2}$, $k_S'$, and $[^1O_2]_{SS}$ can be calculated for any system using equations 2 and 3.  \(16\)

\[\text{Figure 4.5.} \ a) \text{ Rate of 6HP-one formation as a function of FFA concentration for 100 mg film of DWH weathered oil on Gulf of Mexico water irradiated 30 minutes b) Double reciprocal plot allowing determination of singlet oxygen formation and scavenging rates.}\]
\[
\frac{1}{R_p} = \frac{1}{P^1O_2} + \frac{k's}{P^1O_2k_p} \times \frac{1}{[P]} 
\]

(2)

\[
[O_2]_{ss} = \left(\frac{(k's + k'p)}{(k'S \times k'P)}\right) \times R_p 
\]

(3)

Plotting equation 2 as \(1/R_p\) vs \(1/[P]\) (refer to Figure 3.5b) produces a straight line such that the reciprocal of the y-intercept is \(F_{1O2}\), the slope can be used to calculate \(k_s'\), and equation 3 then yields \([O_2]_{ss}\). Our results showed similar trends compared to previous reports \(^{16,79,80}\). Scully and Hoigné stated that humic substances in natural waters produce \(^1O_2\) from only 1% of the sunlight they absorb \(^{80}\). They also mentioned that due to its steady state concentration in natural waters, \(^1O_2\) becomes important as an oxidant for pollutants in natural waters \(^{80}\). Table 4.3 shows the steady state concentration of \(^1O_2\) observed in NP water and GW under irradiated oil films as calculated using equations 2 and 3.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>([O_2]_{ss} (x \times 10^{-12} M)) (HH)</th>
<th>([O_2]_{ss} (x \times 10^{-12} M)) (ZM)</th>
<th>(k_s' (x \times 10^4 s^{-1})) (ZM)</th>
<th>(F_{1O2} (x \times 10^{-8} M/s)) (ZM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP</td>
<td>1.3</td>
<td>1.5 ± 0.1</td>
<td>11.0</td>
<td>16.0</td>
</tr>
<tr>
<td>GW</td>
<td>1.4</td>
<td>1.6 ± 0.2</td>
<td>11.0</td>
<td>16.0</td>
</tr>
</tbody>
</table>

**Table 4.3.** Formation rate of \(^1O_2\), pseudo first order rate constant for scavengers in surface oil/water system, and steady state concentration of \(^1O_2\) for several oil/water systems. 100 mg of oil was placed over 10 mL of water containing varying concentrations of FFA and irradiated for 30 minutes at 1.3 times solar noon intensity (AM 1.5) in a jacketed beaker maintained at 27°C. \([O_2]_{ss}\) calculations labeled HH refers to kinetic model by Haag and Hoigné and ZM refers to kinetic model by Zhou and Mopper. Reported error is one standard deviation for \(N = 3\).

The results for GW and NP water did not show any significant differences, contrary to what was observed in the total singlet trapping experiments (Table 4.2). This result may be due to the fact that at shorter exposure times the differences in these samples are small. In addition, scavenging by natural organic matter could contribute to lowering the \([O_2]_{ss}\) for the GW system.

The second model (HH) we used to determine singlet oxygen concentration was the kinetic model used by Haag and Hoigné \(^{32}\). In this model, it was assumed that when the system
was observed at short exposure times at low concentrations of probe, the probe did not substantially alter the concentration of singlet oxygen. Under these conditions, pseudo first order kinetics can be applied to the loss of the probe in order to calculate \( [^{1}O_{2}]_{ss} \). At low exposure times and low probe concentrations there is minimal trapping so the system is undisturbed. Therefore, equations 4-7 can be applied.

\[
R = k[^{1}O_{2}][FFA] \quad 4
\]

\[
R = k'[FFA] \quad 5
\]

\[
k' = k[^{1}O_{2}]_{ss} \quad 6
\]

\[
[^{1}O_{2}]_{ss} = \frac{k'}{k} \quad 7
\]

In these equations, \( R \) is the rate of FFA reaction with \(^{1}O_{2} \), \( k' \) is the pseudo first order rate constant obtained from the slope of a plot of \( \ln[FFA] \) vs. time, and \( k \) is the second order rate constant (1.2 x10\(^8\) M\(^{-1}\)s\(^{-1}\)) for reaction of FFA with \(^{1}O_{2} \) (NIST.com). Table 4.3 compares the measured singlet oxygen steady state concentrations using the HH and ZM models.

The results from both models give similar values. Such agreement between the models strengthens the reliability of the measured values. Furthermore, the HH model also showed no significant difference between the \( [^{1}O_{2}] \) in NP water compared to GW.

Other studies have reported on singlet oxygen using oil fractions\(^{71}\), including quantum yields of singlet oxygen formed from excitation at 355 nm for diesel oil (0.49 ± 0.04), crude petroleum (0.17 ± 0.04), and fractions at different excitation wavelengths. Tratyek and Hoigne reported \( [^{1}O_{2}]_{ss} \) values in water with dissolved humic acids of 1.25-2.05 x 10\(^{-12}\) M using a filtered medium pressure mercury lamp\(^ {68}\). Zepp et al performed a study for singlet oxygen production in natural waters using 2,5 dimethylfuran (DMF) as a probe\(^ {35}\). They used coastal and inland natural waters from the Southeastern United States and reported \( [^{1}O_{2}]_{ss} \) values as high as 2.2 x 10\(^{-12}\) M\(^ {35}\). These results are very similar to our reported results (Table 3.3), indicating that irradiated thin oil films produce similar singlet oxygen concentrations in the near-oil water as compared to singlet oxygen formed from irradiated DOM. However, our seawater and pure water samples had very low or no DOM, indicating that the oil was the source of singlet oxygen. Haag and Hoigne reported < 2 x 10\(^{-14}\) M for steady state singlet oxygen in irradiated open ocean water\(^ {18}\). The values measured here can be utilized in
predicting rates and products of singlet oxygen mediated oil degradation during solar irradiation. The results from oil on pure water prove that the oil compounds themselves generate singlet oxygen. Since no other source of singlet oxygen was present in these samples, the oil itself must have been the source of singlet oxygen. For oil spilled in open ocean waters, the oil source of singlet oxygen will be much larger than that from DOM since open ocean waters have very low DOM concentrations.

The addition of TiO$_2$ to the system produced comparable results to the experiments without oxide. Table 4.4 shows the results for the oxide systems.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Matrix</th>
<th>[1$^1$O$<em>2$]$</em>{ss}$ (x 10$^{-12}$ M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% TiO$_2$</td>
<td>NP</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>GW</td>
<td>1.3</td>
</tr>
<tr>
<td>9% TiO$_2$</td>
<td>NP</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>GW</td>
<td>1.2</td>
</tr>
<tr>
<td>3% TiO$_2$ NT</td>
<td>NP</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>GW</td>
<td>1.0</td>
</tr>
<tr>
<td>9% TiO$_2$ NT</td>
<td>NP</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>GW</td>
<td>1.2</td>
</tr>
</tbody>
</table>

**Table 4.4.** Steady state concentration of $^1$O$_2$ for surface oil/water systems with varying photocatalyst loading. RSD typically < 10%. HH refers to kinetic model by Haag and Hoigné.

As with the data for moles of singlet oxygen produced (Table 4.2), no significant changes were observed upon the addition of the photocatalysts. These data correlate well with previous studies that used ZnO with FFA. The Zhou and Mopper approach was applied to the systems with oxide, however the results were not consistent with those from the HH model. With oxide, a substantial decrease in the overall formation rate, $F_{1O2}$, and scavenging rate, $k_s'$, were observed. Additional irradiation studies were performed with FFA and TiO$_2$ in the absence of oil in both GW and NP water. The samples with the oxide showed substantial loss of FFA, but no formation of 6HP-one was observed. In the presence of oil, FFA loss was not significantly altered by addition of the oxide. However, we suspect that the formation of 6-HP-
one was altered either by direct photocatalytic degradation or interference with its formation pathway. The competition kinetics model, which was based on 6-HP-one formation, therefore encountered considerable interferences that made it unreliable in the presence of the photocatalysts. The HH model, which relied on loss of FFA, was less sensitive to this interference since FFA reaction with singlet oxygen was much faster than for reaction with hydroxyl radical. Steady state concentrations of singlet oxygen were measured for 6 different oils. Equations 4 -7 for the Haag and Hoigne method were employed to calculate \([1^1\text{O}_2]_{ss}\) for each oil. Table 4.5 compares the measured steady state concentrations.

<table>
<thead>
<tr>
<th>Oil</th>
<th>([1^1\text{O}<em>2]</em>{ss} (\times 10^{-12} \text{ M}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>WDWH</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td>DWH</td>
<td>0.81 ± 0.05</td>
</tr>
<tr>
<td>VAN</td>
<td>0.6 ± 0.2</td>
</tr>
<tr>
<td>HFO #1</td>
<td>0.42 ± 0.05</td>
</tr>
<tr>
<td>HFO #2</td>
<td>0.5 ± 0.2</td>
</tr>
<tr>
<td>HFO #3</td>
<td>0.33 ± 0.02</td>
</tr>
</tbody>
</table>

Table 4.5. Steady state concentrations of singlet oxygen for several different oil samples on GW. Reported error is one standard deviation for N = 3.

The thicker oils, NIST 8505 (VAN), 2717a (HFO #1), 1622e (HFO #2) and 1620c (HFO #3), produced lower steady state concentrations than the thinner oil (DWH). There was a very strong negative correlation between measured aqueous singlet oxygen concentration and absorptivity (R = 0.88, N = 6). These results suggest that singlet oxygen formed at the very surface of the oil where light is absorbed is unlikely to diffuse through viscous oil to reach the aqueous layer. For the more strongly absorbing samples, 90% of 350 nm radiation was attenuated in the first 1 µm of the 60 µm film, while the DWH oil required 9 µm for the same degree of attenuation. Inability of the singlet oxygen to effectively diffuse through the thicker oil layer and react with the FFA probe in the aqueous layer would be a reasonable consequence.
Conclusion

This study proves that oil films produce $^1$O$_2$ that is able to diffuse into the aqueous layer below the oil. The amount of singlet oxygen produced in water under sunlight irradiated DWH surface oil was approximately 1000 times greater than the amount of hydroxyl radical produced in the same systems ($3.7 \times 10^{-7}$ and $4.2 \times 10^{-7}$ moles HO produced in 24 hours of irradiation of oil on GW and NP respectively)\textsuperscript{27}. The results presented here provide a better understanding of the mechanistic and chemical processes occurring in oil systems when exposed to sunlight. It is important to understand these fundamental photochemical processes and use the knowledge presented here to further our understanding of the fate of oil spilled in seawater systems. Oil exposed to sunlight produces both singlet oxygen and hydroxyl radical that can degrade oil in the oil film as well as in the surrounding aqueous layer. Since addition of TiO$_2$ did not alter the $^1$O$_2$ behavior, addition of oxide catalysts to oil in spills will not interfere with singlet oxygen pathways but will contribute to new pathways for oil degradation, such as enhanced hydroxyl radical production. Singlet oxygen is an important intermediate in the degradation of petroleum compounds, especially aromatics, and the concentrations of singlet oxygen reported here will be useful in predicting rates of petroleum degradation.
Abstract

Photochemical production of organic triplets from 6 different compositions of petroleum was measured through the cis-trans isomerization of 1,3 pentadiene in Gulf water. The data correlate very well with previously measured singlet oxygen concentrations. The energies were measured in the range of 280-300 kJ/mol. The photoisomerization state PSS for the petroleum system was reached between 5-6 hours, which is 12 times faster than reported studies for CDOM. The molar absorptivity for each oil sample gave a weak to negative correlation when compared to the pseudo first order rate constant, $k'_{i}$. The weak correlation is due to the fact that not all chromophores are active in producing triplets or those that do not produce triplets are screening light from compounds that do.

Introduction

Photochemical reactions involving dissolved organic matter (DOM) have been widely studied. These reactions are important due to their influence on rates, mechanisms, and products of photochemical processes. These parameters in turn control the fate of pollutants and natural compounds during exposure to sunlight. There are two types of photolysis reactions: direct and indirect. Direct photolysis reactions occur when a chromophore absorbs a photon and reacts as a result. Indirect photolysis occurs when a chromophore...
absorbs a photon to produce a reactive transient (often through energy transfer), which then reacts with a separate species that did not absorb the photon but is subsequently degraded \(^{37}\). The type of reactive transients that are produced from DOM range from reactive oxygen species such as singlet oxygen, hydroxyl radical, and superoxide to non-oxygen species such as carbon centered radicals and excited triplet states \(^{84}\). This study focused on the production of excited triplets from solar exposure of petroleum. Electronically excited states are important because they are capable of reacting with pollutants\(^1\) or with non-pollutant species present in a system. In 2007, Canonica reviewed the previous 15 years of research on triplet induced degradation of organic contaminants in natural water\(^{37}\). He reported that the excited triplet states of colored DOM (CDOM) were the precursors for the oxidative degradation of various contaminants\(^{37}\). This mechanism is important for understanding and predicting the oxidation of pollutants in natural waters\(^{37}\). Bedini et al. used a triplet sensitizer, anthraquinone-2-sulphonate, to study the photoreactivity of CDOM\(^{82}\). They measured the quantum yield and reaction rate kinetics of triplet formation through laser flash photolysis\(^{82}\). Their conclusions from this study indicated that the photochemical mechanism was consistent with a combination of direct phototransformation and sensitized transformation by a photogenerated reactive species\(^{82}\). Zepp et al. performed a kinetics study involving the absorbed light energy transfer from humic substances to organic chemicals in water\(^1\). Zepp et al. reported the involvement of energy transfer from triplet states of different photosensitizers\(^1\). In order to investigate these processes, they used two chemical probes, 1,3-pentadiene and 2,5 dimethylfuran. They studied the photoisomerization of 1,3 pentadiene and photooxidation of 2,5 dimethylfuran as chemical probes in order to assess exited triplet states \(^1\). The study concluded that half the excited triplets formed upon irradiation of natural organic matter had energies of at least 250 kJ/mol, which is enough to transfer energy to PAHs, nitroaromatic compounds, conjugated dienes, and other chemicals \(^1\). Our interest in the formation of excited triplets from petroleum was due to the fact that petroleum contains many PAHs that act as chromophores and the complexity of petroleum is similar to the complexity of DOM. This study focused on the photoisomerization of cis-1,3-pentadiene to trans-1,3-pentadiene similar to the Zepp et al. study in order to measure triplet formation from petroleum as a function of irradiation time. When in contact with an excited triplet, cis-1,3-pentadiene can accept energy from the triplet and be converted into trans-1,3-pentadiene. Conversion from trans to cis is also possible. The common mechanism
for the photochemical cis-trans isomerization is a diabatical process in which the molecule undergoes a torsional relaxation of the double bond with reduced excited state bond order. Under sufficiently long exposure times, the conversion of cis-1,3-pentadiene to trans-1,3-pentadiene reaches a photostationary state (PSS) when the rates of the forward and reverse reactions become equivalent. According to Hammond et al, the photoisomerization of cis-1,3-pentadiene to trans-1,3-pentadiene is a reversible reaction. There have been numerous studies into the photochemical and radiochemical formation of excited triplets and their influence on the isomerization of pentadienes along with other olefins.

PAHs can absorb a photon in the ground single state (S₀) and be excited to the first singlet state (S₁). This excited singlet state can relax back to the ground state or undergo intersystem crossing to the first triplet excited state (T₁). Petroleum photochemistry has been widely studied. Similar to DOM, oil has different compositions depending on the conditions under which it was formed and subsequent changes in the environment. The major chromophores in oil, polycyclic aromatic hydrocarbons (PAHs), are found to be responsible for many direct and indirect photolysis reactions. However, there have been no studies that have measured the production of excited triplet states in petroleum during exposure to sunlight. Our interest in this study was piqued by the nature, role and production of excited triplets in CDOM when exposed to sunlight reported by Zepp et al. This project aimed to study the nature of excited triplets being produced from oil and compare the results to those reported for CDOM in order to see if similar behavior exists.

This study investigated photochemical formation of excited triplets from non-weathered Deepwater Horizon (DWH) oil and weathered DWH (WDWH) crude oil collected from the Deepwater Horizon oil spill that occurred on April 10, 2010. Four NIST standard reference oils (VAN, HFO #1, HFO #2, HFO #3) were also measured for excited triplet formation. All oils were exposed to simulated sunlight while in contact with Gulf of Mexico water and air. This study used the methods and models previously reported for DOM by Zepp et al, and utilized 1,3-pentadiene isomers as chemical probes to measure excited triplet formation from solar irradiated petroleum.
Materials and Methods

Materials

Pure water was obtained by purification of distilled, deionized water with a Barnstead NanopureUV water treatment system (NP water). Gulf of Mexico water (GW) was obtained from the Lumcon and filtered first through a 0.45 µm membrane filter then a 0.2 µm membrane filter (Gelman Science 90 mm Supor-450 and Supor-200 respectively) and stored in the dark at 4°C. The Gulf water had a pH of 7.9 and a salinity of 23 ppt. Weathered DWH oil (surface oil) was collected on May 24, 2010 directly from the surface of the Gulf of Mexico (48.316 N, 89 07.949 W) about 50 miles NW of the Deepwater Horizon site. This oil had risen to the surface through 1500 m of Gulf water and remained on the surface prior to collection. Therefore, volatile compounds and compounds with even modest water solubility had been removed from the weathered DWH oil prior to collection. Oil samples were stored in the dark at 4°C. Additional oil samples included four samples obtained from NIST: SRM 8505 or VAN (V in crude oil), SRM 2171a or HFO #1 (3% S in residual fuel oil), SRM 1622e or HFO #2 (2% S in residual fuel oil), and SRM 1620c or HFO #3 (4% S in residual fuel oil). DWH crude oil from the Macondo well (MC 252) was received from BP (August 2011, chain of custody number 20110803-Tarr-072). cis- and trans 1,3-pentadiene (≥ 97 %) were obtained from Sigma Aldrich and used as received. 200 proof EtOH was obtained from Fisher Scientific.

Sample Preparation

For the probe solution, cis-1,3-pentadiene was dissolved into 100 % EtOH with a final stock concentration of 506 mM. Intermediate standards were prepared in EtOH and finally diluted in Gulf water or NP water to a concentration of 1 mM cis-1,3-pentadiene. Approximately 50 mg of each oil was weighed into the bottom of a 5 mL quartz tube. The tube was sealed using a cap and a Teflon lined septum. The oil samples were chilled for 1 hour at 4°C to increase viscosity and “freeze” the oil in place at the bottom of the tube for easier manipulation in later steps. Freshly prepared aqueous 1 mM cis-1,3-pentadiene was carefully added to each chilled quartz tube containing oil. Due to its high viscosity when chilled, the oil remained at the bottom of the tube and the water remained on top of the oil. The tubes were then sealed with no headspace and inverted so that the less dense oil was at the top of the clear
end of the inverted tube. Tubes were inverted and then placed inside the solar simulator with the top of the oil facing up. Dark controls were prepared in the same manner, then subsequently wrapped in foil. Samples were exposed to simulated sunlight in duplicate for 0.5 h, 3.0 h, 4.5 h, 6.0 h, 12.0 h, and 24 h. The aqueous phase was collected after each irradiation and samples were analyzed by GC for conversion of cis-1,3-pentadiene to trans-1,3-pentadiene.

**Instrumentation**

For photochemical studies, an Atlas CPS+ solar simulator was used (refer to chapter 2 for more details). Photoisomerization products were quantitated by gas chromatography (GC) using an Agilent 6890 series gas chromatograph equipped with a flame ionization detector (FID). A Restek RT-TCEP (1,2,3–tris(2-cyanoethoxy) propane) column, (30 m x 0.25 mm i.d. x 0.4 µm df) was used to separate the cis from the trans pentadiene. The temperature program was isothermal at 40°C for 5 minutes, then ramped up to 60°C at a rate of 5°C/min for 1 minute to elute any residual oil peaks. Helium was used as the carrier gas at a flow rate of 96.1 mL/min, and a 1.0 µL sample volume was used for all injections. The detector temperature was constant at 200°C and the injector temperature was 250°C.

**Results and Discussion**

The results of this study confirm the photochemical production of excited triplet states from petroleum. These results were performed in NP water but no difference was seen between the two matrices therefore only the results for the GW matrix are reported since it is more applicable to the natural environment. Figure 5.1 illustrates the ratio of cis to trans vs. exposure time (h) for the VAN petroleum. At approximately 4.5 hours, the two data points begin to merge together. It is at this point where the rate of cis is equal to the rate of trans or when the system has reached steady state concentration. Zepp et al referred to this as the photostationary state (PSS) and defined it as a point in time when the rate of cis to trans isomerization equals the rate of the reversible reaction. In this study, the PSS state is reached when the rate of formation of excited triplets from precursor compounds in the petroleum is equal to the rate of loss. The isomerization of cis to trans occurs from the transfer of energy from the excited triplet to the cis-pentadiene probe further converting the molecule into trans. The PSS state was reached within approximately 5 hours which is more than 12 times faster.
than the study done by Zepp et al with DOM. The results reported by Zepp showed that under irradiation the photostationary state of humic acid was reached in nearly 67 hours.

Table 5.1 shows the results for the photostationary fraction of trans (T∞) and the respective energies reported in kJ/mol, for each oil sample along with river water samples from the study performed by Zepp et al. The results from our study have been correlated with those obtained by Zepp et al. The energies from the sensitizers reported by Zepp et al were averaged and plotted using a scatter plot. A straight line was obtained and the equation was used to calculate the energies for the trans fraction obtained from the PSS state reached in the current study for each petroleum sample. Since the PSS state for each petroleum sample was reached within 6 hours, the average was calculated from 6, 12 and 24 hour energies. Table 5.1 reports the energy in kJ/mol for each petroleum sample along with the data reported in the Zepp study which was the fraction of trans at the PSS state for river water in natural sunlight. This data was correlated in the same manner as the petroleum samples for comparison.

Figure 5.1. Kinetic data for the isomerization of cis 1,3-pentadiene to trans 1,3-pentadiene vs. irradiation time in Gulf water (1 mM) for VAN crude.
According to the results reported in Table 5.1, the oil produced higher triplet state energies than the reported results for DOM by Zepp et al. According to Zepp et al., energy transfer to trans-1,3 pentadiene becomes slower than to the cis isomer due to lower triplet energy of 250 kJ/mol. In all cases, the petroleum samples produce energies greater than 280 kJ/mol. The 30 kJ/mol difference in energy suggests that the petroleum precursors are effective at producing high energy triplet states therefore the PSS state will be reached at a much faster rate. Table 5.2 reports data for absorptivity, steady state singlet oxygen concentration reported from a previous study, and the pseudo first order rate constant, $k_1'$, for the cis to trans conversion for each oil studied.

### Table 5.1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\infty}$</th>
<th>Triplet State Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VAN</td>
<td>0.516</td>
<td>302</td>
</tr>
<tr>
<td>HFO #1</td>
<td>0.556</td>
<td>287</td>
</tr>
<tr>
<td>HFO #2</td>
<td>0.571</td>
<td>281</td>
</tr>
<tr>
<td>HFO #3</td>
<td>0.547</td>
<td>290</td>
</tr>
<tr>
<td>WDWH</td>
<td>0.554</td>
<td>288</td>
</tr>
<tr>
<td>DWH</td>
<td>0.555</td>
<td>287</td>
</tr>
<tr>
<td>Aucilla River, Fl$^b$</td>
<td>0.638</td>
<td>256</td>
</tr>
<tr>
<td>Suwanee River, Fl$^b$</td>
<td>0.645</td>
<td>253</td>
</tr>
<tr>
<td>Isolated Humus from Wylde Lake, Ontario$^b$</td>
<td>0.635</td>
<td>258</td>
</tr>
</tbody>
</table>

**Table 5.1.** Oil and river water photostationary states in isomerization of 1,3-Pentadiene in Gulf water and river water respectively.

$^a$ Fraction of trans-1,3-Pentadiene at photostationary state using sunlight.

$^b$ Results in river water samples obtained from Zepp et al.
According to Zepp et al, the pseudo first order rate constant, $k'_{i}$, represents the sum of the rate constants for the isomerization of the cis to trans conversion and the trans to cis conversion\(^{1}\). The $k'_{i}$ values were calculated based on an integrated rate expression for the photoisomerization reported by Zepp et al for DOM\(^{1}\). Equation 5.1 shows this expression, where $T_{\infty}$, $T_{0}$, $T_{t}$ represent the fraction of diene that was trans at the photostationary state and $t$ represents irradiation time\(^{1}\).

\[
\ln \left( \frac{T_{\infty} - T_{0}}{T_{\infty} - T_{t}} \right) = k'_{i}t
\]

Equation 5.1

Figure 5.2 shows a plot of previously measured steady state [$^{1}\text{O}_2$] vs. $k'_{i}$ for each oil. This graph illustrates the direct correlation between the formation of triplets and the concentration of singlet oxygen with the exception of one oil sample (shown in white). The data correlate very well with data obtained from a previous study measuring singlet oxygen production in petroleum. Consequently, we infer that the production of $^{1}\text{O}_2$ and its relationship with $k'_{i}$ is due to the fact that both of these transient species have similar photochemical pathways. Since

<table>
<thead>
<tr>
<th>Oil</th>
<th>Path Length Required for 90% Attenuation at 350 nm (μm)</th>
<th>$a_{300}$ (cm(^{-1}))</th>
<th>$a_{350}$ (cm(^{-1}))</th>
<th>$a_{400}$ (cm(^{-1}))</th>
<th>$[^{1}\text{O}<em>2]</em>{ss}$ (x10(^{-12})) M</th>
<th>$k'_{i}$ excited triplets</th>
</tr>
</thead>
<tbody>
<tr>
<td>WDWH</td>
<td>5.7</td>
<td>5531</td>
<td>1757</td>
<td>742</td>
<td>1.2 ± 0.12</td>
<td>1.25</td>
</tr>
<tr>
<td>DWH</td>
<td>9</td>
<td>3958</td>
<td>1115</td>
<td>456</td>
<td>0.81 ± 0.05</td>
<td>0.97</td>
</tr>
<tr>
<td>VAN</td>
<td>1.7</td>
<td>13170</td>
<td>5922</td>
<td>3175</td>
<td>0.57 ± 0.18</td>
<td>0.70</td>
</tr>
<tr>
<td>HFO #1</td>
<td>1.2</td>
<td>18070</td>
<td>8406</td>
<td>4325</td>
<td>0.42 ± 0.05</td>
<td>0.45</td>
</tr>
<tr>
<td>HFO #2</td>
<td>1</td>
<td>21690</td>
<td>9849</td>
<td>5053</td>
<td>0.51 ± 0.18</td>
<td>0.54</td>
</tr>
<tr>
<td>HFO #3</td>
<td>1</td>
<td>20415</td>
<td>10408</td>
<td>5362</td>
<td>0.33 ± 0.02</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Table 5.2. Absorptivity data, singlet oxygen concentrations and photostationary rate constant, $k'_{i}$ for excited triplet formation from petroleum.
the pathway to a low energy triplet state is slow ($10^{-11}$ to $10^{-6}$ sec), the type of molecules that go through this phenomenon are typically large and conjugated. The amount of energy needed for a molecule to undergo intersystem crossing ranges from 170 to 290 kJ/mol\textsuperscript{88}. The type of molecules that meet these conditions are PAHs, which are found in high concentrations in petroleum.

![Figure 5.2](image_url)\textsuperscript{89}

**Figure 5.2.** Represents the relationship between $k'_i$ vs. singlet oxygen concentration. The red data point is the only oil that did not correlate to singlet oxygen concentration (HFO #3).

When a molecule absorbs light of an appropriate wavelength, the molecule undergoes a change in its electronic state from ground state to an excited electronic state (Refer to Figure 1.3). In the excited electronic state there are a number of vibrational levels that exist. Once the molecule reaches this state, which is its first excited singlet state ($S_1$), it can go through a range of decay processes to transfer the energy it received upon absorption. There are a number of important pathways the molecule can go through to relax back down to its ground state. There are radiative and non-radiative processes. In this paper we are focusing on the non-radiative relaxation called intersystem crossing. In order for a molecule to undergo intersystem crossing
it must go from its lowest excited singlet state to the lowest excited triplet state. This process involves the coupling of vibrational energy states from the singlet state to the triplet state. If the molecule has overlap in the energy levels between the first excited state and the triplet state, one of its electrons can undergo a change in its spin state. A change in spin state leads to the conversion of a singlet state to a triplet state and is a spin-forbidden process. In the first excited triplet state the molecule has several pathways. It can undergo external conversion and react with $^3$O$_2$ forming $^1$O$_2$ or it can transfer energy from its excited triplet state to a sensitizer and/or quencher. Other pathways can occur but our focus is on the formation of excited triplet states and the transfer of this energy to cis-1,3 pentadiene. Figure 5.3 shows a plot for absorptivity vs. triplet formation ($k'_i$). Three wavelengths were investigated, 300 nm, 350 nm and 400 nm ($R^2 = 0.57, 0.52, 0.54$ respectively). There is a weak, negative correlation between $k'_i$ and absorptivity for all wavelengths, which concludes that not all the chromophores are active in producing triplets or those that do not produce triplets are screening light from the compounds that do.

![Figure 5.3](image)

**Figure 5.3.** $k'_i$ vs. absorptivity plot showing weak, negative correlation at 300 nm (■), 350 nm (■), and 400 nm (■) for each oil.
Conclusion

This research presents the first study that probes into the formation of excited triplets formed after solar irradiation of petroleum. The results presented are on average 30 kJ/mol higher than the energies reported for CDOM. Also, this study showed a strong correlation between the production of $^1$O$_2$ measured in a separate study and the formation of excited triplets. This study is important in order to understand the fate of petroleum as well as the type of reactive transients produced when it is exposed to sunlight. This data will provide a greater understanding of the fate of oil after exposure to the sunlight. This information will be directly applicable to modeling of oil in the environment, to predicting the bioavailability and toxicity of oil as it is exposed to sunlight, and in improving remediation efforts.
CHAPTER 6. SUNLIGHT CREATES OXYGENATED SPECIES IN WATER-SOLUBLE FRACTIONS OF DEEPWATER HORIZON OIL

Abstract

Macondo Well Oil from the Deepwater Horizon (DWH) rig was mixed with pure water and irradiated with simulated sunlight. After irradiation, the water-soluble organics (WSO) from the dark and irradiated samples were extracted and characterized by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Liquid-liquid extraction yielded two fractions from dark and irradiated water/oil mixtures: acidic WSOs (negative-ion electrospray (ESI)), and base/neutral WSOs (positive-ion ESI) coupled to FT-ICR MS to catalogue molecular-level transformations that occur to Macondo-derived WSOs after solar irradiation. The most abundant heteroatom class detected in the irradiated WSO acid fractions correspond to molecules that contain five oxygens (O₅), while the most abundant acids in the dark samples contain two oxygen atoms per molecule (O₂). Higher-order oxygen classes (O₅ – O₉) were abundant in the irradiated samples, but < 1.5 % relative abundance in the dark sample. The increased abundance of higher-order oxygen classes in the irradiated samples relative to the dark samples indicates that photooxidized components of the Macondo crude oil become water-soluble after irradiation. The base/neutral fraction showed decreased abundance of pyridinic nitrogen (N₁) concurrent with an increased abundance of N₁O₅ classes.
after irradiation. The predominance of higher-order oxygen classes indicates that multiple photochemical pathways exist that result in oxidation of petroleum compounds.

**Introduction**

Anthropogenic release of crude oil challenges sensitive marine ecosystems, and have increased as offshore oil production moves to deeper waters. Oil spills such as the DWH blowout cause ecosystem disruption, environmental damage, and negative human health effects. Despite the extensive study of oil spills, there is still a large void in understanding how sunlight affects the fate and transport of oil. Previous studies used conventional techniques such as GC or GC/MS to characterize the effects of sunlight on fate and transport of petroleum in the environment. D’Auria, et al. used headspace SPME-GC rather than GC-MS, to identify a larger number of compounds that were formed in Basilicata crude oil as a result of irradiation. However, these techniques are limited to compounds that are volatile below 400 °C, and are unable to identify polar or non-volatile compounds typically found in weathered oil. In order to obtain a detailed understanding of the fate and transport of oil after exposure to sunlight, a more comprehensive technique such as FT-ICR MS is needed.

Advanced analytical techniques for the characterization of polar and nonvolatile compounds can identify photochemical transformations that occur to petrogenic molecules at the molecular level. Comprehensive two dimensional gas chromatography (GC×GC) and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) have recently been applied to study oil spills. Here, we combined FT-ICR MS with electrospray ionization (ESI) to target polar chemical functionalities and catalogue molecular changes through photochemical transformation.

The explosion of the *Deepwater Horizon* oil rig occurred on April 20, 2010 and released an estimated ~5 million barrels of light, sweet crude oil from the Macondo well into the Gulf of Mexico over 87 days. Since the spill, numerous studies have addressed the fate of the Macondo oil and origin and characterization of oxygenated species as a result of weathering. However, these studies provided a limited ability to differentiate between biodegradation and photodegradation. Previous studies have targeted oil molecules that partition into water. Stanford *et al.* identified molecular formulas of water-soluble species present in South American and Medium Arabian crude oils by FT-ICR MS.
Fathalla and Andersson observed formation of oxygenated products upon irradiation of polycyclic aromatic sulfur heterocycle oil fractions. However, this work used a mercury lamp and added anthraquinone at 4.5% by weight as a photosensitizer. Consequently, their results may differ somewhat from those obtained under environmental conditions. Another study focused on atmospheric photochemistry related to the Deepwater Horizon spill.

To date, there have not been any studies reporting on the changes in molecular composition of the water-soluble oil species after solar irradiation. Several studies report the formation of oxygenated compounds that occur with extent of weathering, but report the combined effects of photochemistry and biodegradation or photochemical transformations of crude oil, but not at the molecular level. The compositional complexity of crude oil makes ultrahigh resolution FT-ICR mass spectrometry the only technique capable of resolving and identifying components within crude oil and its water-soluble fraction at the molecular level. Here, we compared compositional changes that occurred to water-soluble organic compounds derived from the Macondo well parent oil, and catalogued molecular transformations that occurred due to irradiation with simulated sunlight. WSOs from solar irradiated oil contain an increased abundance of multiheteroatomic oxygen classes compared to non-irradiated (dark) WSO fractions. This result suggests that solar-driven processes result in rapid oxidation of parent oil components, and play a large role in the ultimate fate and transport of oil spilled in the environment.

**Materials and Methods**

**Materials**

Pure water was obtained by purification of distilled, deionized water with a Barnstead NanopureUV water treatment system (NP water). Dichloromethane-GC grade (99.9%), H₂SO₄ (93-98%), NaOH pellets (97.0%) were obtained from Fisher Scientific. Nylon Membrane Filters (nylaflow, 0.45µm, 47 mm) obtained from Pall Life Sciences. HPLC grade methanol and toluene were purchased from JT Baker (Phillipsburg, NJ). Ammonium hydroxide (28% ammonia in water), and formic acid, were obtained from Sigma-Aldrich (St. Louis, MO). All reagents were used as received.
Simulated Solar Irradiation

Samples were irradiated with constant stirring in 250 mL jacketed glass beakers kept at 27 °C. An Atlas CPS+ solar simulator was used (refer to Chapter 2 for more details).

Sample preparation

This study utilized the method previously reported by Stanford, et al. After irradiation, samples were allowed to stand for 24 h in a separatory funnel to allow the oil and water to separate. The water was then removed and placed in a clean separatory funnel and allowed to stand for an additional 24 hours so that any residual oil would separate. After removal from this funnel, the collected water (~90 mL) was made basic (~pH 12) with NaOH and then was extracted with 20 mL of DCM four times yielding the base/neutral fraction. The DCM washes were pooled and evaporated. The water phase was filtered to remove and metal hydroxides/oxides that had precipitated. The clarified water was acidified (~pH 2) with H$_2$SO$_4$ and extracted four-fold with 20 ml of DCM yielding the acid fraction. The DCM washes were pooled and evaporated. The base/neutral or acid residues were dissolved separately into toluene to a final concentration of 1 mg/mL. The samples were further diluted to 250 µg/mL with equal parts (v/v) of methanol. Crude oil from the Macondo well (MC 252) (received from BP, August 2011, chain of custody number 20110803-Tarr-072) was placed in the amount of 10 mL over 100 mL of pure water in a jacketed beaker and stirred in the dark for 7 days at 27 °C. After 7 days, the equilibrated sample was then exposed to simulated sunlight at 27 °C while stirring for 12 hours (equivalent to 3 days of average solar irradiation in the Northern Gulf of Mexico). A dark control was prepared in the same manner, but not irradiated. Both dark and irradiated blank pure water samples (no oil) were prepared and analyzed in the same manner as other samples. After separating the oil and water, aqueous samples were then extracted to collect a base/neutral fraction and an acid fraction according to previously reported methods. Prior to FT-ICR MS analysis, a stock solution (1 mg/mL) that was further diluted to yield a final concentration of 125-250 µg/mL in equal parts (v/v) toluene:methanol spiked with 1% NH$_4$OH (negative ESI) or 1% formic acid (positive ESI). Refer to Appendix A4 Chapter 6 for FT-ICR MS conditions and parameters.
Results and Discussion

Acid Extract

No appreciable signals were observed for dark and irradiated blank pure water samples (no oil). Figure 6.1 shows negative-ion ESI broadband spectra of the dark and irradiated acid extracts.

Figure 6.1: Negative-ion ESI FT-ICR mass spectrum of the dark and irradiated WSO acid extracts from the Macondo well oil. The top-right corner shows a 0.4 Da mass-expanded window at m/z 343. A 2-fold increase in the number of identified peaks and a relative shift in the most abundant peaks to lower mass defect is observed for the irradiated sample and are indications of increased compositional complexity and increased oxygen heteroatom content, respectively, after irradiation.

A 0.4 Da mass-expanded insert at m/z 343 shows several broad trends associated with the composition of WSOs extracted from the irradiated sample relative to the sample kept in the dark. The mass spectrum of the WSOs extracted from the dark sample has 47 peaks greater than 6σ RMS baseline noise at m/z 343, while the irradiated extract has 81. The nearly 2-fold
increase in the number of identified peaks at a single nominal mass in the irradiated extract can be attributed to increased compositional complexity of WSOs leached from the crude as a result of photooxidation. Moreover, a shift of the most abundant peaks to lower mass defect is observed in the irradiated extract relative to the dark extract. The relative shift to lower mass defect in the irradiated extract is a result of the addition of oxygen atoms which have a negative mass defect.

The most abundant heteroatom class for the dark acid fraction samples consisted of O$_2$ species that correspond to carboxylic acid moieties (i.e., compounds with the formula C$_x$H$_y$O$_2$), which is in agreement with previous reports.$^{108, 122, 123}$ After irradiation, the most abundant heteroatom class was O$_5$. The irradiated samples were dominated by O$_3$, O$_4$, O$_5$, O$_6$, and O$_7$ heteroatom classes, while the same classes in the dark sample were of much lower abundance (refer to Figure 6.2 discussed below). An increase in the relative abundance of higher-order oxygen classes occurred with irradiation. The abundance of multiheteroatomic oxygenated compounds could suggest that compounds are more reactive after initial oxidation, and are more readily oxidized. However, future studies will target the oxidation pathway more iteratively to identify intermediate chemical transitions.

Elemental compositions derived from FT-ICR MS characterization can be presented as color-coded isoabundance contour plots of double bond equivalents (DBE, or number of rings or double bonds to carbon, DBE = C – h/2 + n/2 +1$^{124}$) versus carbon number to compare compositional changes within a heteroatom class. Figure 6.2 shows DBE versus carbon number plots for O$_2$-O$_7$ classes detected in the water-soluble acid fraction without irradiation (left) and after irradiation (right).
A strong correlation between DBE and carbon number appears for each compound class that correlates to a polymeric structural motif, evident by the increase in DBE that occurs with each oxygen atom per molecule, in agreement with previous reports for highly-oxygenated biofuels\textsuperscript{125} and petroleum compounds detected in produced water\textsuperscript{126}. 

\textbf{Figure 6.2.} Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for $O_2$ - $O_7$ classes without irradiation (left) and after irradiation (right). The carbon number and DBE for the most abundant species in each compounds class are given in red.
Plots of relative abundance vs DBE and relative abundance vs DBE-O are provided (Figures 6.3 and 6.4) to illustrate that photooxygenation resulted in solubilization of high DBE species.

![Graph showing relative abundance vs DBE for dark and irradiated samples.](image)

**Figure 6.3:** Relative abundance vs. DBE for the dark and irradiated DWH WSO acid fractions analyzed by (−) ESI FT-ICR MS. The shift to higher DBE for the irradiated sample is the result of increased water solubility of these species, primarily due to oxygenation.
Compositional Comparison: DBE versus Carbon Number Images for $O_x$ Classes

The most acidic compounds in petroleum correspond to the naphthenic (non-aromatic) acids (carboxylic acids), which correspond to $O_2$ species with DBE 1-3. For $O_2$ and $O_3$ classes, compounds with DBE 5-15 and $C_{10} - C_{30}$ were detected from dark Macondo-derived water-soluble acids, which were previously attributed to aromatic acids by Stanford et al. However, those reported water-soluble species were derived from heavy, high total acid number (TAN) crude oils that is not directly comparable to the low TAN Macondo oil. Higher-order oxygen classes ($O_4-O_7$) contain compounds with higher DBE values after irradiation, but are less than 1% relative abundance without irradiation.

After irradiation, low molecular weight naphthenic acids (DBE 1-3) were observed in $O_2$ class, but $O_3$ compounds spanned a wide carbon number range ($C_{10}-C_{30}$) with DBE values between 1-20. The $O_4$ compounds extended to $C_{35}$; $O_5$ to $C_{40}$; $O_6$ to $C_{45}$; and $O_7$ to $C_{50}$. Compounds that contained multiple oxygens per molecule were more abundant after irradiation, and therefore photochemical pathways increase the polarity of petroleum.

Figure 6.4: Relative abundance vs. DBE-O for the dark and irradiated DWH WSO acid fractions analyzed by (-) ESI FT-ICR MS. Compared to Fig. 6.3, the dark and irradiated samples show a much more similar pattern. This result is consistent with the conclusion that the irradiated sample contained higher oxygen content. The plot above suggest that subtraction of $O$ substantially accounts for the differences in the WSO for dark and irradiated samples.
compounds and increase the water-solubility of Macondo oil-derived hydrocarbons. Water-soluble organics produced from photo-oxygenation of crude oil indicates that photochemistry is capable of producing highly toxic, water-soluble aromatic species that are made bioavailable.\textsuperscript{44,57} Importantly, oxidation occurred across a wide range of DBE values suggesting that aromatic structures, and homologues, are susceptible to photochemical transformation, as previously reported.\textsuperscript{57} However, it is unknown from this study whether oxidation occurs along alkyl chains, or at aromatic/naphthenic cores that exist as homologous series in petroleum. Future studies will target structural analysis with fragmentation studies through tandem MS. The wide DBE and carbon number distribution of O\textsubscript{4}-O\textsubscript{10} species and increased relative abundance after irradiation further supports the conclusion that oxidation proceeds in series, and that once oxidized, these compounds are more susceptible to further oxidation. Further analysis to characterize intermediate pathways will be the subject of future studies.

\textbf{Van Krevelen Diagrams for Compound Class Comparison after Irradiation}

Because FT-ICR mass spectral analysis provides elemental composition assignment for organic compounds \([\text{C}_\text{c}\text{H}_\text{h}\text{N}_\text{n}\text{O}_\text{o}\text{S}_\text{s}]\), van Krevelen diagrams have been applied to visualize complex organic samples to compare H/C and O/C ratios for major chemical compound classes.\textsuperscript{49} Furthermore, aromaticity indices can be calculated and applied to visualize differences in the degree of unsaturation between samples.\textsuperscript{123} Figure 6.5 compares H/C and O/C ratios for oxygen-containing compounds (O\textsubscript{1}-O\textsubscript{10}) in the water-soluble acid fraction by negative-ion ESI without irradiation (a) and after irradiation (b), and the difference (c).
Water-soluble compounds exposed to irradiation exhibit lower H/C ratios, and higher O/C ratios than dark compounds. Figure 6.5c presents the elemental composition of acidic compounds that are unique to the dark (green) and irradiated (blue) samples. Dark compounds correspond to O/C ratios < 0.2 and H/C ratio > 1 (higher degree of saturation), while irradiated compounds convert to higher O/C and lower H/C ratio (more aromatic). Oxidation occurred
over a wide range of saturation and O/C ratio, and irradiation increased the O/C ratio to create highly oxygenated compounds, in agreement with previous reports.\(^8\)

**Heteroatom Class Distribution As a Function of Irradiation**

Heteroatom class distributions derived from negative-ion ESI FT-ICR MS can readily identify global changes in relative abundance between irradiated and non-irradiated water soluble acidic species. Figure 6.6a compares the relative abundance for O\(_1\)-O\(_{10}\) water-soluble acidic species with and without irradiation.

![Graph: Relative Abundance of Heteroatom Classes](image)

**Figure 6.6.** a) Negative mode ESI-FT-MS of acid fraction for the dark (black) vs. irradiated (red) samples modified with NH\(_4\)OH for the O\(_x\) series; b) Negative mode ESI-FT-MS of acid fraction for the dark (black) vs. irradiated (red) samples modified with NH\(_4\)OH for the N\(_1\)O\(_x\) series. Relative abundance is normalized to all observed species for each sample.

Without irradiation, the O\(_2\) class is the most abundant, but after irradiation, higher-order oxygen classes (O\(_4\)-O\(_{10}\)) increase in abundance. This result provides additional evidence that photochemical reactions increase the number of oxygens per molecule, thus increasing the water-solubility of oil-derived compounds, in agreement with previous studies on heavy crude oil.\(^{20}\) Figure 6.6b highlights N\(_1\)O\(_x\) classes detected in water-soluble acid fractions. The monoheteroatomic N\(_1\) class detected in negative-ion ESI FT-ICR MS that corresponds to five-
membered ring nitrogen (pyrrolic) was detected at ∼ 3.8% relative abundance without irradiation, but barely detected above the baseline after irradiation, while N$_1$O$_4$-N$_1$O$_9$ compounds increased in abundance after irradiation. This finding agrees with the increased oxygenation after irradiation, and indicates that photochemistry occurs to oil-derived water-soluble species; however, the ionization efficiency of O$_2$ species is much higher than N$_1$ classes, and future studies will focus on other ionization techniques to target specific nitrogen chemistry.

The Macondo Well oil has been well-characterized at the molecular level by FT-ICR mass spectrometry. McKenna et al. developed a database which provides a detailed molecular characterization of the Macondo Well oil by negative-ion ESI. Common core structures in petroleum ionized by negative-ion ESI include phenols, fluorenes, carbazoles, carboxylic acids, and indoles. After irradiation, nonpolar parent molecules undergo photooxidation, incorporate oxygen to hydrophobic cores, increase in polarity, and become water soluble. The previous study compared the parent oil to a weathered tar ball and reported the increased abundance of oxygen-containing compounds across the same mass range after weathering. Here, water-solubility limits the characterization to the most polar compounds, as evident by the higher abundance of O$_5$-O$_7$ classes.

**N$_1$O$_x$ Acidic Classes**

Figure 6.7 shows van Krevelen plots for the N$_1$-N$_{10}$ heteroatom classes before (6.7a) and after (6.7b) irradiation.
Figure 6.7. van Krevelen plots for the $N_1$-$NO_{10}$ classes of the acid fraction by (-) ESI for a) dark sample, b) irradiated sample, and c) subtraction plot showing compounds unique to the dark or irradiated sample.

The same trend occurs as discussed for $O_x$ species, and nitrogen compounds that contain more oxygens ($N_1O_4 - N_1O_5$) increased in abundance with irradiation. Figure 6.7 highlights oxidation trends that occur to $N_1O_x$ compounds over a wide range of H/C ratios and aromaticity indices. Figure 6.7c shows the detected acidic $N_1$-$N_1O_9$ compounds ionized by negative-ion ESI that are unique to dark or irradiated samples as a plot of H/C vs. O/C and the corresponding data for H/C vs. N/C are presented in Figure 6.8.
**Figure 6.8.** van Krevelen diagram of the acid fraction by (-) ESI FT-ICR MS for the N-NO$_9$ heteroatom classes. Green circles correspond to formulas only assigned to the dark sample and blue triangles correspond to those only assigned after irradiation.

Formulas unique to the irradiated sample correspond to N/C ratios between 0.02 and 0.11, illustrating the increased polarity (and thus water-solubility) of higher N/C Macondo-derived hydrocarbons after irradiation. DBE vs. carbon number plots for N$_1$O$_3$-N$_1$O$_6$ are displayed in Figure 6.9 and highlight the increase in DBE and carbon number that occur with irradiation.
For the dark sample, the N$_1$ class was the most abundant nitrogen class and represented 3.9% of detected species with DBE values ranging from 5 to 36 and carbon numbers from C$_{14}$ – C$_{60}$. N$_1$O$_1$ species were also prevalent in the dark WSOs with a relative abundance of 2.3%. This class had DBE values from 1 to 20 and spanned C$_{11}$ – C$_{54}$. After irradiation, a shift to higher oxygenation was observed, and N$_1$O$_4$ became the most abundant nitrogen species detected in negative-ion mode. N$_1$O$_5$ through N$_1$O$_7$ species were also present at greater than 1% relative abundance. For the irradiated sample, the N$_1$O$_4$ species ranged in DBE from 1-21.

**Figure 6.9.** Isoabundance-contour plots of double bond equivalents (DBE) vs. carbon number of (-) ESI FT-ICRMS data for water soluble acidic compound classes (N$_1$O$_3$ through N$_1$O$_6$) from the irradiated oil (right) vs. dark oil (left). The average carbon number and DBE is highlighted in the top-right corner of each plot.

**Compositional Comparison: DBE versus Carbon Number Images for N$_1$O$_x$ Classes**

For the dark sample, the N$_1$ class was the most abundant nitrogen class and represented 3.9% of detected species with DBE values ranging from 5 to 36 and carbon numbers from C$_{14}$ – C$_{60}$. N$_1$O$_1$ species were also prevalent in the dark WSOs with a relative abundance of 2.3%. This class had DBE values from 1 to 20 and spanned C$_{11}$ – C$_{54}$. After irradiation, a shift to higher oxygenation was observed, and N$_1$O$_4$ became the most abundant nitrogen species detected in negative-ion mode. N$_1$O$_5$ through N$_1$O$_7$ species were also present at greater than 1% relative abundance. For the irradiated sample, the N$_1$O$_4$ species ranged in DBE from 1-21.
and C\textsubscript{10} – C\textsubscript{44}, the N\textsubscript{1}O\textsubscript{5} species spanned DBE 1-22 and C\textsubscript{11}-C\textsubscript{43}, the N\textsubscript{1}O\textsubscript{6} spanned DBE 1-23 and C\textsubscript{12} – C\textsubscript{44}, and the N\textsubscript{1}O\textsubscript{7} spanned DBE 3-26 and C\textsubscript{12} – C\textsubscript{44}.

As observed for O\textsubscript{x} classes, compounds that contained multiple oxygens per molecule were more abundant after irradiation, and therefore photochemical pathways increased the polarity of nitrogen containing petroleum compounds and increase the water-solubility of these compounds in Macondo well oil. Also similar to the O\textsubscript{x} classes, oxidation occurred across a wide range of DBE values suggesting that aromatic structures, and homologues, are susceptible to photochemical transformation, as previously reported\textsuperscript{57}. The wide DBE and carbon number distribution of N\textsubscript{1}O\textsubscript{5}-N\textsubscript{1}O\textsubscript{7} species and increased relative abundance after irradiation suggest that oxidation proceeds in series, and that once oxidized, these compounds are more susceptible to further oxidation.

**Base/Neutral Fraction**

**N\textsubscript{1}O\textsubscript{x} Basic Classes**

Basic compounds in petroleum detected by positive-ion ESI typically have pyridinic functional groups\textsuperscript{110} which correspond to N\textsubscript{1} species (most abundant molecular formula DBE 15, C\textsubscript{39}) in the parent Macondo well oil.\textsuperscript{2} Figure 6.10 shows a DBE vs. carbon number plot for the N\textsubscript{1} heteroatom classes containing 0 to 4 oxygen atoms in the dark and irradiated base fractions from Macondo derived water soluble bases observed by positive-ion ESI (corresponding van Krevelen plots are shown in Figure 6.11).
Figure 6.10. Isoabundance-contour plots of double bond equivalents (DBE) vs. carbon number from FT-ICR MS data for water-soluble basic compound classes ($\text{C}_x\text{H}_y\text{N}_1$, $\text{C}_x\text{H}_y\text{N}_1\text{O}_4$) from the dark oil (left) vs. irradiated oil (right).
After irradiation, a significant decrease in the relative abundance of the N₁ class of the irradiated sample (1.9%) was observed in comparison to the dark sample (6.1%). For the N₁ class, the DBE values ranged from 5-23 for the dark and 5-14 for the irradiated samples. Furthermore, the N₁O₃ species extended to DBE 1-22 and C₄₀ in the dark and DBE 1-15 and C₃₄ in the irradiated sample. The most abundant N₁ class in the irradiated sample was N₁O₄, providing further evidence that N₁ compounds were photooxidized during irradiation. N₁O₃-N₁O₇ classes spanned over a wide carbon range and DBE values from 5 to 20. The N₁O₃
compounds extended to C$_{42}$; N$_1$O$_4$ to C$_{39}$; N$_1$O$_5$ to C$_{38}$; N$_1$O$_6$ to C$_{36}$; N$_1$O$_7$ to C$_{34}$. As reported by McKenna, *et al.* the type of compounds typically found in the parent Macondo Well oil in positive-ion ESI are pyridines, quinolines, benzo(f)quinolines, and isoquinolines.$^2$ Once these compounds are photooxidized, they become water soluble. As with the O$_x$ classes, nitrogen containing species (N$_1$O$_x$ classes) showed multiple oxygens per molecule after irradiation, demonstrating that the basic nitrogen containing species were also susceptible to multiple oxidations as the result of photochemical pathways, resulting in enhanced water solubility of the basic nitrogen containing compounds. The types of oxygenated compounds ionized by positive-ion ESI are likely ketone, aldehyde, alcohol, ether, and ester derivatives of the parent oil compounds$^2$. However, since greater relative abundance of oxygenated species was observed by negative-ion ESI, we expect that photoproducts are predominantly carboxylic acids.

Figure 6.12 shows a heteroatom class graph of relative abundance of the C$_x$H$_y$N$_1$O$_z$ base fraction species by positive-ion ESI. The N$_1$ species in the irradiated sample showed an overall decrease in the relative abundance and an increase in oxygenated N$_1$ species relative to the dark samples. These results are likely due to photooxygenation of the N$_1$ species.

**Figure 6.12:** Positive-ion ESI FT-ICR MS of base fraction for the dark (black) vs. irradiated (red) samples modified with formic acid for the N$_1$O$_x$ series. Relative abundance is normalized to all observed species for each sample.
Aeppli, *et al.* showed the formation of oxygenated hydrocarbon species from weathered oil in a study published in 2012.\textsuperscript{106} The oxygenated hydrocarbon fraction of weathered Macondo oil observed in that study was made up of more than 50% of the weathered sample mass.\textsuperscript{106} That report proposed that the accumulation of these species was due to formation through biodegradation and photooxidation.\textsuperscript{106} Furthermore, they stated that the molecular level transformations of petroleum hydrocarbons led to increasing amounts of oxyhydrocarbons.\textsuperscript{106} The results depicted in the current study correlate well with the Aeppli study in that photooxidation was demonstrated to play a major role in the formation of oxygenated compounds. Furthermore, in our study we observed the direct formation of oxygenated compounds as a result of exposure to simulated sunlight. We also hypothesize that once a molecule becomes oxygenated, its ability to be further oxygenated is still high. This conclusion is reasonable since O\textsubscript{4} and O\textsubscript{5} species were the most abundant in negative-ion ESI spectra of the irradiated acid fractions and compounds with as many as 10 oxygens were readily detectable. For positive-ion ESI spectra, multiply oxygenated species were also prevalent in the irradiated oil.

While photochemical transformations of the oil itself were apparent, it is also likely that water soluble oil compounds were subject to further photodegradation in the aqueous phase. Initial oxidation could result in increased water solubility, and further oxidation is likely to take place in the aqueous phase. The color and mass of residue from the water soluble fraction was greater when oil and water were irradiated together than when only the water soluble oil compounds were irradiated without oil present. Furthermore, evidence of increase dissolved organic carbon was also observed when oil/water systems were irradiated. The photochemical processes occurring in the aqueous phase are the subject of ongoing studies. Nevertheless, it is clear that sunlight results in substantial oxygenation of oil compounds, resulting in increased water solubility of the photoproducts.

**Conclusion**

This research presented data for the water soluble compounds formed after solar irradiation of Macondo oil. Identification of the compounds formed provides a greater understanding of the fate of oil after exposure to the sun. This information will be directly applicable to modeling of oil in the environment, to predicting the bioavailability and toxicity
of oil as it is exposed to sunlight, and in improving remediation efforts. Further study is needed to determine the effects of seawater on these observed photochemical processes.
CHAPTER 7. Photochemistry of oils originating from different sources. Effect of viscosity and density on the photoproduction of oxygenated species using FT-ICR MS.

Abstract
Oils from multiple sources were mixed with seawater and irradiated with simulated sunlight. The water-soluble organics (WSO) from the dark and irradiated samples were extracted and characterized by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Liquid-liquid extraction yielded two fractions from dark and irradiated water/oil mixtures: acidic WSOs (negative-ion electrospray (ESI)), and base/neutral WSOs (positive-ion ESI). These fractions were analyzed by FT-ICR MS to catalogue molecular-level transformations that occurred to oil-derived WSOs after solar irradiation. In the WSO acid fraction, O$_2$-O$_4$ species predominated in the dark fraction whereas the irradiated fraction showed a distribution shift from O$_2$-O$_{10}$ centered around O$_4$-O$_5$. An increase in the overall abundance in the higher order oxygen classes in the irradiated samples of multiple oils indicates that photooxidized compounds become water soluble after irradiation. A wider range of oxygenated compounds were observed in the WSO acid fraction of oils with higher API gravity.

Introduction
There have been many studies reporting on the photooxidation of oil\textsuperscript{11, 107, 118, 129-135}. Once oxidized, petroleum compounds become more water-soluble and more bioavailable in an ecosystem. Numerous studies have reported on the toxicity of these water-soluble compounds, which have been reported to be naphthenic acids\textsuperscript{131, 136-141}. Therefore, it is important to identify these water-soluble compounds in order to understand their physical and chemical properties and their role in the environment. The characterization and molecular composition for crude oil itself has been extensively studied\textsuperscript{6, 7, 10, 57, 95, 103-105}. Radovic \textit{et al} demonstrated compositional changes of thin oil films as a result of photooxidation\textsuperscript{142}. Experiments were performed by exposing thin oil films to natural or simulated sunlight and then analyzed using
Griffiths et al. performed a study investigating the effect of simulated light on crude oil films. Experiments were performed for 938 h using a UV light source and a SoLux source, which closely resembles the solar spectrum. It was reported that a large increase in the abundance of oxygenated species was observed for the irradiated samples especially with the SoLux lamp, using Fourier transform ion cyclotron mass spectrometry (FT-ICR-MS) coupled with atmospheric pressure photoionization (APPI). Both of these studies utilized simulated or natural sunlight to assess the impact of light on the photooxidation of neat oil; however, they did not study the release of photoproducts into water as a result of crude oil films exposed to simulated light. There is limited information on the molecular composition of water-soluble organic (WSO) species produced as a result of photoxidized petroleum due to the inability to differentiate between biodegradation and photodegradation for the origin and characterization of oxygenated species. Stanford et al. identified molecular formulas of water-soluble species present in South American and Medium Arabian crude oils by FT-ICR MS.

In March of 1989, a 987-foot tank vessel, Exxon Valdez, hit a reef in Prince William Sound Alaska, releasing 10.8 million gallons of North Slope Crude oil. At this time, this was the largest and worst oil spill to occur in the Nation. Since Exxon Valdez there have been many more large-scale oil spills. In 2007, the Cosco Busan oil spill occurred in the San Francisco Bay when a vessel collided with the Oakland Bay Bridge. The oil released from this spill was a heavy fuel oil (HFO) and about 200,000 Liters of HFO were released into the San Francisco Bay. The explosion of the Deepwater Horizon oil rig occurred on April 20, 2010 and released an estimated 5 million barrels of light, sweet crude oil from the Macondo well into the Gulf of Mexico over 87 days. Since the Macondo spill, numerous studies have addressed the fate of the Macondo oil and origin and characterization of oxygenated species as a result of weathering. This study provides detailed molecular composition of the water-soluble species photochemically produced from multiple compositions of oil after solar irradiation in seawater systems. Here, we compared compositional changes that occurred to water-soluble organic compounds derived from the Macondo well oil, Noonan, and HFO oils and catalogued molecular transformations that occurred due to irradiation with simulated sunlight in Gulf water. The purpose of testing different oils is to build a molecular composition database as well as to investigate the effect of
viscosity and elemental composition of these different oils on the photoproduction of WSO. Furthermore, understanding the photochemical processes that occur to different sources of oil can help understand the photochemical fate of other compositions of oils. In 1985, Payne and Philips published a review on the photochemistry of petroleum\textsuperscript{147}. They reported results for photochemical effects on viscosity for light versus heavy crude oil lenses on water\textsuperscript{147}. It was found that the more viscous oils contracted about 10\% in the lens diameter when exposed to light\textsuperscript{147}. This change to the oil lens occurred within a few hours after light exposure and was attributed to the inability of the photooxidation products formed in the oil-air interface to diffuse through the heavy crude oil layer and to be removed from the oil-water interface\textsuperscript{147}. The current study explored the effect of seawater vs. pure water on the production of water-soluble species in the Macondo well oil. Since seawater is more polar, it has been shown to accommodate fewer WSO species when compared to pure water\textsuperscript{108}. Stanford et al reported that seawater accommodated water-soluble species due to electrostriction and the strong interaction between the ions and water molecules\textsuperscript{108}. Headley \textit{et al} demonstrated through negative ion FT-ICR MS that salt interactions affected the distribution of organic acid components found in processed water from oil sands bitumen samples collected from northern Alberta, Canada\textsuperscript{148}.

The objective of this study was to understand the photochemical processes of different types of petroleum in Gulf water, specifically identifying the molecular composition of the compounds produced in the water as a result of photodegradation. The aim of this study was to provide a database for molecular level transformations for each oil in a simulated aquatic environment. This information can be used to improve response and remediation efforts should future spills occur.

**Experimental Section**

**Materials:**

Seawater was obtained from the Gulf of Mexico was obtained from the Louisiana Universities Marine Consortium and was filtered through a 0.45 \textmu M glass fiber filter. Dichloromethane-GC grade (99.9\%), H\textsubscript{2}SO\textsubscript{4} (93-98\%), NaOH pellets (97.0\%) were obtained from Fisher Scientific. Nylon membrane filters (Nylaflow, 0.45\,\mu m, 47 mm) obtained from Pall Life Sciences. HPLC grade methanol and toluene were purchased from JT Baker.
Ammonium hydroxide (28% ammonia in water) and formic acid were obtained from Sigma-Aldrich (St. Louis, MO). All reagents were used as received.

**Sample Preparation**

Five petroleum samples were analyzed in this study. Oil from the Macondo well-MC 252 (DWH), (received from BP, August 2011, chain of custody number 20110803-Tarr-072), Noonan well #586 (NPO) originated from a reservoir located in the Gulf of Mexico and three standard reference materials SRM 8505 (VAN), 2717a (HFO#1) and 1622e (HFO #2) were obtained from the National Institute of Science and Technology (NIST). The DWH and Noonan oils were pipetted in the amount of 10 mL over 100 mL of Gulf of Mexico (GW) water (pH 8) in a borosilicate jacketed beaker (see Figure A4). The SRM oils were heated to 50°C then weighed in the amount of 10 g. Due to their high viscosity, the SRM oils were dispersed in 1 mL of toluene, then poured over 100 mL of GW water. The toluene was evaporated to dryness prior to the equilibration step. Each oil/water sample was then stirred in the dark for 7 days at 27 °C. After 7 days, the equilibrated sample was then exposed to simulated sunlight at 27 °C while stirring for 12 hours (equivalent to 3 days of average solar irradiation in the Northern Gulf of Mexico). Details for simulated sunlight are provided in Chapter 2. A dark control for each oil was prepared in the same manner but not irradiated. Both dark and irradiated Gulf water samples (no oil) were prepared and analyzed in the same manner as other samples. After separating the oil and water, aqueous samples were then extracted to collect a base/neutral fraction and an acid fraction according to previously reported methods.

Prior to FT-ICR MS analysis, the WSO extracts were prepared at a concentration of 125-250 µg/mL in equal parts (vol:vol) toluene:methanol spiked with 1% NH₃OH (negative ESI) or 1% formic acid (positive ESI). Ionization source conditions and detailed experimental conditions are discussed in Appendix A.

**Simulated Solar Irradiation**

Samples were irradiated with constant stirring in 250 mL jacketed beakers (Figure A5) kept at 27 °C. An Atlas CPS+ solar simulator was used (refer to Chapter 2 for details).
**Sample preparation:**

This study utilized the method previously reported by Stanford, et al.\textsuperscript{108} After irradiation, samples were allowed to stand for 24 h in a separatory funnel to allow the oil and water to separate. The water was then removed and placed in a clean separatory funnel and allowed to stand for an additional 24 hours so that any residual oil would separate. After removal from this funnel, the collected water (~90 mL) was made basic (~pH 12) with NaOH and then was extracted with 20 mL of DCM four times yielding the base/neutral fraction. The DCM washes were pooled and evaporated. The water phase was filtered to remove and metal hydroxides/oxides that had precipitated. The clarified water was acidified (~pH 2) with H\textsubscript{2}SO\textsubscript{4} and extracted four-fold with 20 ml of DCM yielding the acid fraction. The DCM washes were pooled and evaporated. The base/neutral or acid residues were dissolved separately into toluene to a final concentration of 1 mg/mL. The samples were further diluted to 250 µg/mL with equal parts (v/v) of methanol. Prior to FT-ICR MS analysis, samples were modified using 1% (by volume) formic acid (positive ESI) or spiked with 1% (by volume) ammonium hydroxide (negative ESI) to ensure efficient protonation/deprotonation.

**Results and Discussion**

**Sample Selection**

Five oils were selected for this study based on their different properties and relationship to past oil spills or heavily exported oils. Table 7.1 lists each oil along with their physical and chemical properties. American Petroleum Institute gravity or API gravity is a measure of how dense petroleum is compared to water.\textsuperscript{149} (Refer to Table 7.1 for list of each oil and their properties). Macondo well oil (DWH) is a sweet crude oil and was spilled into the Gulf of Mexico following the explosion of the rig on the Deepwater horizon Platform in 2010. Noonan oil (NPO) is a light crude with high concentrations of perylene, which gives it a light blue color from the fluorescence of perylene. This oil was chosen due to its similar properties in comparison to DWH oil. The NPO oil was recovered from a reservoir also located in the Gulf of Mexico. SRM 2717a (HFO #1) and SRM 1622e (HFO #2) are heavy fuel oils (HFO) high in sulfur with HFO #1 containing 3% sulfur by mass and HFO #2 containing 2% sulfur by mass. These two oils were chosen because they best represent the HFO oil from the Cosco Busan oil spill that occurred in the San Francisco Bay in 2007. Also, tanker vessels contain
large fuel reserves that can become damaged and leak into the environment if the fuel containers are compromised. The last oil, SRM 8505 (VAN), is a heavy Venezuelan crude oil. This oil was chosen because the oil reserves in Venezuela are among the largest in the world and fourth largest exporter to the United States (20,000 barrels since 2014\textsuperscript{150}). The oil is exported by tanker vessels and contains high amounts of Vanadium (390 ± 10 µg/g). Since 1970, there have been 5.75 million tons of oil spilled due to tankers despite the increase in tanker safety\textsuperscript{151}. Due to the heavy exportation of this oil by tanker vessels, a basic understanding of the compounds produced through photochemical reactions in aquatic systems is important. The photochemistry of these oils was investigated through the production of water soluble organics (WSO) in Gulf of Mexico water (GW).

<table>
<thead>
<tr>
<th>Oil</th>
<th>API Gravity</th>
<th>%N</th>
<th>%S</th>
<th>Viscosity (mm\textsuperscript{2}/s) @50°C</th>
<th>Density (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DWH</td>
<td>35.2</td>
<td>0.69</td>
<td>0.261</td>
<td>4.627</td>
<td>0.849</td>
</tr>
<tr>
<td>NPO</td>
<td>28.7</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>0.883</td>
</tr>
<tr>
<td>HFO #1</td>
<td>11.22\textsuperscript{b}</td>
<td>0.405\textsuperscript{b}</td>
<td>2.147\textsuperscript{b}</td>
<td>282.0\textsuperscript{b}</td>
<td>0.991\textsuperscript{b}</td>
</tr>
<tr>
<td>HFO #2</td>
<td>9.2\textsuperscript{b}</td>
<td>N/A</td>
<td>2.999\textsuperscript{b}</td>
<td>776.9\textsuperscript{b}</td>
<td>1.006\textsuperscript{b}</td>
</tr>
<tr>
<td>VAN</td>
<td>12.0</td>
<td>N/A</td>
<td>N/A</td>
<td>1915\textsuperscript{b}</td>
<td>0.986\textsuperscript{b}</td>
</tr>
</tbody>
</table>

Table 7.1: API and elemental composition for each oil.
\textsuperscript{b}. Data obtained from NIST.com
N/A-Not Available

**Isoabundance Contour Plots**

Elemental compositions derived from FT-ICR MS characterization can be presented as color-coded isoabundance contour plots of double bond equivalents (DBE, or number of rings or double bonds to carbon, DBE = C − H/2 + N/2 + 1\textsuperscript{124}) versus carbon number to compare compositional changes within a heteroatom class. These plots are graphical images which are formed from heteroatom classes in order to sort thousands of chemical formulas and compare each sample class\textsuperscript{2}. These images can illustrate compositional changes between samples, e.g. dark vs. irradiated. DBE distribution and compound classes are reported for peaks with a
magnitude higher than baseline noise of $6\sigma$. The relative abundance of each peak was calculated compared to the total signal for all peaks, and it is dependent on the abundance of other species. The isoabundance plots presented in the main text are combined class plots for each series to illustrate global changes across all O$_x$ and N$_1$O$_x$ species. The individual isoabundance plots for each of the O$_x$ classes are in Appendix A, figures A6-A15 and for N$_1$O$_x$ Figures A16-A23. No significant signals were observed for dark and irradiated Gulf water samples (no oil). The compositional changes observed for the acid fractions from DWH, NPO, HFO #1, HFO #2 and VAN analyzed using (-) ESI FT-ICR MS are compared and discussed below.

**DWH and NPO**

O$_x$ classes. Figure 7.1a shows combined isoabundance plots for the O$_1$-O$_{10}$ classes for the DWH (top) and NPO (bottom) WSO acidic species. The dark plots are shown on the left and the irradiated plots are shown on the right. For both oils there was a noticeable increase in the size and shape of the distribution between irradiated vs. dark samples. The dark DWH isoabundance plot showed a distribution ranging from DBE 1-14 and carbon number ranging from C$_{11}$-C$_{25}$. Once exposed to light, the distribution expanded from DBE 2-18 and C$_{12}$-C$_{35}$. The compositional changes observed for the dark NPO acid fraction also showed an expanded distribution with a DBE ranging from 2-5, and carbon number ranging from C$_{10}$-C$_{20}$. For the irradiated NPO acid fraction, a shift in the distribution was observed at DBE 3-10 and carbon number to C$_{11}$-C$_{30}$. Refer to Appendix A (figures A6-A15) for the individual isoabundance plots for each of the O$_x$ classes.

For both the DWH and NPO, an increase in the number of oxygens occurred once the samples were exposed to light. This result was observed in previous studies using DWH oil on pure water.
**Figure 7.1:** Combined class plots for the (a) Oₓ class and (b) N₁Oₓ class from the acid water-soluble fraction analyzed in (-) ESI in GW for DWH (top) and NPO (bottom).

**N₁Oₓ classes.** Figure 7.1b represents the global class plots for the N₁Oₓ species observed in the acid fraction analyzed using (-) ESI for DWH (top) and NPO (bottom). The compositional changes for the dark acid fraction in DWH showed a DBE range of 5-15 and Carbon number ranging from C₁₀-C₂₅. The irradiated acid fraction for DWH had a distribution of DBE ranging from 6-15 and a slightly wider carbon number expansion observed from C₁₅-C₃₀. Without exposure, the NPO dark acid fraction DBE ranged from 3-11 and carbon number C₁₁-C₂₅. After exposure, the NPO DBE shifted to DBE 4-16 and the carbon number expanded to C₃₃. The individual isoabundance plots for N₁Oₓ classes are in Appendix A, Figures A16-A23.
van Krevelen Diagrams

In order to visualize complex organic samples, van Krevelen diagrams have been applied to compare H/C and O/C ratios for major chemical compound classes\(^\text{49}\). The O/C ratio is separated along the horizontal axis and the H/C ratio is separated along the vertical axis for each observed molecular formula.\(^\text{152}\) As the DBE increases, a decrease in the H/C ratio is seen, which represents increasing aromaticity\(^\text{123,152}\). These diagrams are especially useful for FT-ICR mass spectral analysis since they provide elemental composition assignment for organic compounds \([C\text{\_}n\text{H\_}m\text{N\_}n\text{O\_}o\text{S\_}s]\). To visualize differences in the degree of unsaturation between samples, aromaticity indices can be calculated and applied\(^\text{123}\). The van Krevelen diagrams enable samples that are processed differently to be distinguished by the location of each point on the plots\(^\text{49}\).

O\(_x\) Classes. Figure 7.2 compares H/C and O/C ratios for oxygen containing compounds (O\(_1\) - O\(_{10}\)) in the water-soluble acid fraction in the DWH (top) and NPO (bottom) samples without irradiation (a) and (d) and after irradiation (b) and (e), and the difference (c) and (f) respectively. Water-soluble compounds exhibit lower H/C ratios and higher O/C ratios than the dark compounds after exposure. This can be observed by the increase in the number of points in the center of mass in figure 7.2 (b) and (e). Chemical formulas assigned for the O\(_x\) species are plotted for the H/C vs. O/C ratio for each elemental composition observed in the dark (Figure 7.2a) and irradiated (Figure 7.2b). Figure 7.2c illustrates the elemental composition of acidic compounds that are unique to dark (green) and unique to irradiated (blue) samples. For the DWH, dark compounds correspond to O/C ratios <0.2 and H/C ratios <1 (higher degree of saturation), while irradiated compounds convert to higher O/C and lower H/C ratios (more aromatic). This trend is seen in the irradiated acid fraction (Figure 7.2b). The NPO acid fraction produced the most dramatic changes observed after irradiation. Figure 7.2 (bottom) illustrates the elemental composition for the NPO dark acid fraction (7.2d), after irradiation (7.2e) and the difference plot (7.2f). The dark acid fraction had fewer points on the pots when compared to the irradiated. The difference plot highlights the compounds unique to dark (green points) and unique to irradiated (blue points). The increase in the number of compounds that are unique to the irradiated suggests that there was an increase in the number of oxygenated species produced after light exposure. Irradiation increased the O/C ratio to
create highly oxygenated compounds, and oxidation occurred over a wide range of saturation and O/C ratio. This result is in agreement with other reports. The same trends were observed as discussed for the O species: Nitrogen compounds that contain more oxygen (N\textsubscript{1}O\textsubscript{3}-N\textsubscript{1}O\textsubscript{9}) increased in abundance with irradiation. Figure 7.3 emphasizes oxidation trends that occurred to N\textsubscript{1}O\textsubscript{x} compounds over a wide range of H/C ratios and aromaticity indices.

Figure 7.2. van Krevelen plots for the DWH (top) and NPO (bottom) O\textsubscript{1}-O\textsubscript{10} classes of the acid fraction by (-) ESI in GW for a) and d) dark sample, b) and e) irradiated sample, and c) and f) subtraction plot showing compounds unique to the dark or irradiated sample, respectively.

N\textsubscript{1}O\textsubscript{x} classes. Figure 7.3 shows the van Krevelen plots for the N\textsubscript{1}-N\textsubscript{1}O\textsubscript{10} heteroatom class before (7.3a,d) and after (7.3b,e) irradiation for DWH and NPO respectively. The same trends were observed as discussed for the O\textsubscript{x} species: Nitrogen compounds that contain more oxygens (N\textsubscript{1}O\textsubscript{3}-N\textsubscript{1}O\textsubscript{9}) increased in abundance with irradiation. Figure 7.3 emphasizes oxidation trends that occurred to N\textsubscript{1}O\textsubscript{x} compounds over a wide range of H/C ratios and aromaticity indices. Figure 7.3c and 7.3f show detected acidic N\textsubscript{1}-N\textsubscript{1}O\textsubscript{10} compounds ionized by negative-ion ESI unique to dark (green) or unique to irradiated (blue) samples as a function of H/C vs. O/C. The DWH results are presented on the top and NPO results are presented on the bottom. For both samples, there is a noticeable difference when comparing the dark (a and d) and irradiated (b and e) samples. There is a wide distribution of new compounds from H/C 0.5-1.8 and O/C 0.0-2.0.

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0.05-0.5 formed as a result of irradiation when compared the sample without irradiation. Figure 7.3 (c and f) show many newly formed N$_1$-NO$_{10}$ species in the irradiated sample for DWH (top) and NPO (bottom) respectively.

**Figure 7.3.** van Krevelen plots for the DWH (top) and NPO (bottom) N$_1$-NO$_{10}$ classes of the acid fraction by (-) ESI in GW for a) and d) dark sample, b) and e) irradiated sample, and c) and f) subtraction plot showing compounds unique to the dark or irradiated sample, respectively.

### Heteroatom Class Distribution as a Function of Irradiation

Heteroatom class distributions derived from negative-ion ESI FT-ICR MS can readily identify global changes in relative abundance between irradiated and non-irradiated water-soluble acidic species. Figure 7.4 and 7.5 compare the relative abundance (RA) dark acid fraction (a) and the irradiated acid fraction (b) for the O$_1$-O$_{10}$ and N$_1$O$_1$-N$_1$O$_{10}$ Gulf water-soluble species for all oils respectively.

**O$_x$ Class.** Figure 7.4 highlights the %RA vs heteroatom class graph for the O$_x$ class for all oils. The most abundant heteroatom class found in the dark DWH (blue) and NPO (orange) acid fraction was O$_4$. The DWH O$_4$ had a relative abundance of 10.6%, an average DBE 8 and average carbon number of C$_{20}$. The most abundant species in the dark NPO was O$_4$ (31.5 %
RA) with an average DBE of 5 and average carbon number of C<sub>20</sub>. In the irradiated DWH acid fractions, O<sub>4</sub> remained the most abundant (8.9% RA); however a decrease in relative abundance was observed when compared to the dark acid fraction. The irradiated DWH acid fraction showed enrichment in the O<sub>5</sub> - O<sub>10</sub> species when compared to the dark acid fraction. For the irradiated NPO acid fraction, O<sub>4</sub>S<sub>1</sub> was the most abundant at 12.6% RA with a DBE = 5 and C<sub>19</sub> followed by O<sub>5</sub> with a DBE = 8 and C<sub>21</sub> respectively. Additionally, a decrease in the relative abundance of the O<sub>4</sub> class (7.9%) was observed when compared to the dark NPO acid fraction. The O<sub>5</sub> - O<sub>9</sub> species dominated in the irradiated NPO acid fractions having relative abundances ranging from 1.5% to 9.3%. The enhancement of O<sub>2</sub>, O<sub>3</sub> and O<sub>4</sub> species in the water soluble classes observed for both oils, was reported in previous studies using different sources of oil and NPW<sup>152,153</sup>. The focus of this study is to observe these changes in seawater systems. This will provide environmentally relevant data to contribute to oil spill modeling and databases. These compounds are typically carboxylic acids or low molecular weight fatty acids as reported by Stanford et al<sup>108</sup>.

**Figure 7.4.** a) Negative mode ESI-FT-MS of acid fraction for the dark samples modified with NH<sub>4</sub>OH for the O<sub>x</sub> series; b) Negative mode ESI-FT-MS of acid fraction for the irradiated samples modified with NH<sub>4</sub>OH for the O<sub>x</sub> series. Relative abundance is normalized to all observed species for each sample.
**N₁Oₓ Classes.** Figure 7.5 shows the relative abundance vs. heteroatom class graph for the dark (a) vs. irradiated (b) acid fraction samples collected in (-) mode ESI using FT-ICR MS for both the DWH (blue) and NPO (teal) crudes. The relative abundance for each series in the DWH (molecular formula CₓHᵧN₁Oₓ) are higher for the N₁O₁, N₁O₆ - N₁O₈ classes in the irradiated acid fraction than in the dark acid fraction. In the dark DWH acid fraction, the most abundant heteroatom class is N₁O₃ (4.2 % RA). The irradiated DWH acid fraction increased in relative abundance for the N₁O₃ (6.6 %) and the oxygenation increased. Similar to the Oₓ heteroatom class graph (figure 7.4), the N₁Oₓ classes are in higher relative abundance when compared to the dark and there is a shift in distribution to higher oxygenated species as a result of irradiation. In the dark NPO acid fraction, N₁O₁-N₁O₅ species were not detected above 0.5% relative abundance. However, an increase in N₁O₄-N₁O₉ species was observed in the irradiated when compared to the dark. The monoheteroatomic N₁ class that corresponds to five-membered ring nitrogen (pyrrolic) was detected at ~ 3.8% relative abundance without irradiation in pure water¹⁵³, but barely detected above the baseline in seawater, while N₁O₁-N₁O₁₀ compounds increased in abundance after irradiation (Figure 7.5b) in both the DWH and NPO fractions.
Figure 7.5. a) Negative mode ESI-FT-MS of acid fraction for the dark samples modified with NH$_4$OH for the N$_1$-N$_1$O$_x$ series; b) Negative mode ESI-FT-MS of acid fraction for the irradiated samples modified with NH$_4$OH for the N$_1$-N$_1$O$_{10}$ series. Relative abundance is normalized to all observed species for each sample.

These findings agree with the increased oxygenation after irradiation, and indicates that photochemistry occurs to oil-derived water-soluble species. However, the ionization efficiency of O$_2$ and O$_4$ species is much higher than N$_1$ classes, and future studies will focus on other ionization techniques to target specific nitrogen chemistry. Also, the data illustrate that seawater N$_1$ classes need to have more oxygen atoms in order to become water-soluble due to the increased polarity of seawater when compared to pure water.
HFO #1 and HFO #2

Isoabundance Plots

HFO #1 and HFO #2 are heavy fuel oils, which contain high concentrations of sulfur. The API density for each oil is reported in Table 7.1. In comparison to DWH, both oils have a higher density and a much higher viscosity (Table 7.1). Therefore it is inferred that the diffusion of reactants (e.g. O\textsubscript{2}) into the oil and of photoproducts into the water will be inhibited. Payne \textit{et al} reported that the more viscous oils hinder the diffusion of the compounds produced as a result of photochemistry, reducing their ability to enter the water\textsuperscript{147}.

\textbf{O\textsubscript{x} classes}. Figure 7.6a highlights the compositional changes occurring between the dark (left) and irradiated (right) DBE vs. Carbon Number plots for HFO #1 (top) and HFO #2 (bottom). For the dark HFO #1 acid fraction, the DBE ranges from 1-8 and carbon number C\textsubscript{12}-C\textsubscript{18}. The irradiated acid fraction shows a more pronounced and wider distribution from DBE 1-18 and C\textsubscript{10}-C\textsubscript{32}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.6.png}
\caption{Combined class plots for the (a) O\textsubscript{x} class and (b) N\textsubscript{1}O\textsubscript{x} from the acid water-soluble fraction analyzed in (-) ESI in GW for HFO #1 (top) and HFO #2 (bottom).}
\end{figure}

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**\( \text{N}_1\text{O}_x \text{ Classes.} \)** Figure 7.6b represents the global plot for the \( \text{N}_1\text{O}_x \) series for HFO #1 (top) and HFO #2 (bottom). An increase in the number of oxygens per nitrogen molecule was observed in the irradiated acid fraction. For HFO #2, there were few differences observed between the dark vs irradiated from \( \text{N}_1\text{O}_1\text{-N}_1\text{O}_3 \) species, but more changes were observed for higher oxygenated species (\( \text{N}_1\text{O}_4\text{-N}_1\text{O}_8 \)). This could be due to the increased viscosity of the HFO #2 and the inability of the oxygenated compounds to diffuse through the oil into the water. The compositional changes observed for both HFO #1 and HFO #2 in the dark acid fraction showed DBE ranging from 1-12 and carbon number from \( \text{C}_{10}\text{-C}_{20} \). The irradiated fraction showed an increase in oxygen across the \( \text{O}_1\text{-O}_9 \) series for both oils (DBE 1-16, \( \text{C}_{10}\text{-C}_{30} \)).

**van Krevelen diagrams**

**\( \text{O}_x \text{ Classes.} \)** Figure 7.7 shows the van Krevelen diagrams for HFO #1 (top) and HFO #2 (bottom). For both oils, there is a shift to higher O/C ratio after irradiation. The difference plots (7.7c) do not show a substantial amount of new compounds formed as a result of irradiation. These oils exhibited a much lower composition of WSO \( \text{O}_x \) species than the DWH and NPO sample. These oils are much more viscous and dense (Table 7.1) than the DWH and NPO oil. Therefore, it is suspected that these properties play a role in the lack of WSO \( \text{O}_x \) species produced as a result of photooxidation.
Figure 7.8 shows the van Krevelen plots for N$_1$-N$_{10}$ heteroatom class before (7.8a and 7.8d) and after (7.8b and 7.8e) irradiation for HFO #1 (top) and HFO #2 (bottom) respectively. In the HFO #1 dark acid fraction (Figure 7.8a), there is a wide distribution from H/C 2.0 and O/C 0.1-0.6 when compared to the irradiated Figure 7.8b. The difference plot, Figure 7.8c, does not show many new compounds unique to the irradiated sample when compared to the dark sample. For HFO #2 (Figure 7.8d) the dark acid fraction has a higher density of unique molecular formulas in the H/C 0.5-1.5 and O/C 0.1-0.3 range when compared to the irradiated sample (7.8e). The difference plot (7.8f) shows more compounds unique to the irradiated sample than the dark sample. In comparison to the DWH and NPO oils, there were fewer compounds produced in these two heavy fuel oils as a result of photooxidation of petroleum.
Figure 7.4 represents the % RA vs. heteroatom class graph for the dark (a) and irradiated (b) acid fractions reported for HFO #1 (purple) and HFO #2 (teal). The most abundant heteroatom class found in the dark acid fraction for HFO #1 and HFO #2 was O₄ (11.2 % RA and 11.1 % RA respectively). The O₄ species was the most abundant in the irradiated acid fraction however decreased in the overall relative abundance when compared to the dark and irradiated DWH acid fraction. Unlike the DWH oil, highly oxygenated species found in the irradiated samples were only about 1% higher than in the dark acid fraction for both oils.
**N$_1$O$_x$ Classes.** Figure 7.5 illustrates the trends in oxygenation for the N$_1$O$_x$ compounds in the dark (a) versus irradiated (b) samples. For HFO #1 (purple) and HFO #2 (teal), the most abundant class for the dark acid fraction was N$_1$O$_3$ (2.6 % RA and 4.9 % RA respectively). For the samples exposed to light there was a two-fold increase in abundance for the N$_1$O$_5$-N$_1$O$_8$ species.

**VAN**

**Isoabundance Plots**

**O$_x$ Classes.** Venezuelan crude oil, VAN, is high in vanadium (390 ± 10 µ/g). Table 7.1 reports the properties for this crude. Figure 6.9a represents the combined DBE vs. carbon number plots for the O$_x$ class from the acid WSO fraction analyzed in (-) ESI in GW. The left column represents compounds detected in the dark and the right column represents compounds detected in the irradiated sample. In comparison to the other four oils tested in this study, VAN showed the fewest differences between the dark vs. irradiated. The distribution in the dark and irradiated fractions showed DBE ranging from 2-8 and carbon number C$_{10}$-C$_{22}$. Despite the lack of WSO products formed, this data set still reveals information regarding the effect of photochemistry on oils with high viscosity. This information is important when considering basic process and mechanisms that are implicated in the photodegradation of oil. Previous studies have found a decrease in singlet oxygen concentrations using this oil compared to DWH.$^{154}$
**Figure 7.9**: Combined class plots for the (a) $O_x$ class and (b) $N_1O_x$ from the acid water-soluble fraction analyzed in (-) ESI in GW for VAN.

**$N_1O_x$ Classes.** Figure 7.9b shows the combined class plot for the VAN $N_1O_x$ class. The $N_1O_3$ species was the only nitrogen containing compound observed in the dark acid fraction. In the irradiated acid fraction, $N_1O_3$ and $N_1O_4$ were observed in low abundance (<1%). Since this oil is very viscous and dense (refer to table 7.1), the low yield of photoproducts in the aqueous phase was expected. Less photoproducts were produced, likely as a result of the high viscosity limiting the ability of the photoproducts to diffuse into the Gulf water.

**van Krevelen Diagrams**

Due to its viscosity, it is inferred that the VAN oil did not allow for efficient diffusion of oxygen into the oil to participate in photooxidation reactions or the diffusion of the photoproducts from the oil to the water was inhibited. The lack of photoproducts is apparent in the overall number of compounds produced and therefore a van Krevelen diagram was not possible for this data set.
Heteroatom Class Graph

The most abundant heteroatom class found in the dark acid fraction was \( \text{O}_3\text{S}_1 \), with a relative abundance of 26.3% (molecular formula \( \text{C}_x\text{H}_y\text{O}_3\text{S}_1 \)). Although the average DBE of 5 and carbon number of \( \text{C}_{18} \) were unchanged between dark and irradiated samples, the relative abundance of the \( \text{O}_3\text{S}_1 \) class increased to 33.3 % after irradiation. Figure 7.4 compares the dark (a) and the irradiated (b) for the VAN crude. In the dark the \( \text{O}_2 \) had the highest relative abundance (15.4 %) and the irradiated showed a decrease in the \( \text{O}_2 \) (9.3 %). There was a small shift to the right observed for more oxygenated compounds in the irradiated; however, it is inferred that the high viscosity prevented the diffusion of these compounds. Ongoing studies will determine the type of oxygenated compounds in the oil layer as a result of irradiation.

Stanford et al observed the same results in negative-ion ESI in that the nitrogen containing species are water soluble only if an oxygen is present in combination with a pyrrolic group\(^{152}\). These groups must contain functional groups that strongly bond to hydrogen atoms in the water\(^{152, 155, 156}\). Compounds that contained multiple oxygens per molecule were more abundant after irradiation, and therefore photochemical pathways increased the polarity of petroleum compounds and increased the water-solubility of oil-derived hydrocarbons. This result provides additional evidence that photochemical reactions increase the number of oxygens per molecule, thus increasing the water-solubility of oil-derived compounds, in agreement with previous studies on heavy crude oil\(^20\). However, the ionic strength of the Gulf water plays a role in the overall solubility of these compounds in the aqueous phase, and more oxygens are required per molecule in order for the photoproducts to be water soluble in the higher polarity salt water compared to pure water. Furthermore, the role of viscosity and density have a direct impact on the photochemistry for each of the oils. The DWH and NPO oils showed the most differences between the dark and irradiated. The HFO oils provided details regarding the effect of viscosity and API on the diffusion of photoproducts. The VAN oil provided the most evidence for these conclusions in the fact that it had the highest viscosity and API density out of all of them thus produced the least amount of WSO species as a result of photodegradation.

Positive-Ion ESI was also investigated, however two broad distributions of ions were observed in the mass spectra, suggesting the presence of dimers. A 40 W Synrad CO\(_2\) laser
was used in attempt to break up the dimers; however, even high laser doses (20 J per pulse), could not break up the apparent dimers. This result has been observed in previous studies analyzing sodiated, protonated and potassium bound sulfoxide dimers\textsuperscript{122, 152}.

**Conclusion**

This research presented data for petroleum compounds made water soluble in Gulf water due to solar irradiation. Of all the oils studied, the high perylene NPO oil showed the most dramatic results for the irradiated acid fraction compared to the non-irradiated fraction. The least interesting was the highly viscous VAN oil. The heteroatom class graphs showed that after irradiation, higher-order oxygen classes (O\textsubscript{6}-O\textsubscript{9}) increase in abundance and a shift to the right in the distribution is observed for both the O\textsubscript{x} and N\textsubscript{1}O\textsubscript{x} series for all oils in this study. The photochemical production of water soluble organics varied dramatically across different oil samples. A general trend of increasing numbers of water soluble compounds with decreasing oil density or viscosity was observed. The impact of photochemistry on the fate of spilled oil will therefore be highly dependent on the density and viscosity of the oil. Another possible explanation is penetration of light into the aqueous phase. The thicker oils would be less likely to break up into droplets and would therefore better maintain a light blocking film above the water. The toxicity of oil photoproducts will also therefore depend on the properties of the oil. The oils selected for this study are representative of previous oil spills or heavily exported oils. Furthermore, there is limited data that distinguishes between biotic and abiotic modifications as a result of photochemical formation of oxygenated species. The knowledge gained from this study will broaden our understanding of the photochemical processes when these oils are subjected to aquatic systems. This information will be directly applicable to modeling of oil in the environment, to predicting the bioavailability and toxicity of oil as it is exposed to sunlight, and in improving remediation efforts.
Chapter 8. Oxygenated Species in Photochemically Produced Water-soluble Fractions of Deepwater Horizon Oil Show Loss of High MW Species Over Time

Abstract

Macondo Well Oil from the Deepwater Horizon (DWH) rig was separately mixed with pure water and Gulf of Mexico water then exposed to simulated sunlight for 12 h, 24 h, 48 h and 120 h. After irradiation, the water-soluble organics (WSO) from the dark and irradiated samples were extracted and characterized by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Liquid-liquid extraction yielded two fractions from dark and irradiated water/oil mixtures: acidic WSOs (negative-ion electrospray (ESI)), and base/neutral WSOs (positive-ion ESI) coupled to FT-ICR MS to catalogue molecular-level transformations that occur to Macondo-derived WSOs after solar irradiation. As the irradiation time increased, a loss of DBE and number of carbons was observed for the $O_x$ series. In the 12 h GW water sample, the upper edge of the $O_x$ series distribution started at DBE 17 and C$_{30}$ and after 120 h contracted to DBE 14 and C$_{25}$. The increased abundance of higher-order oxygen classes in the irradiated samples relative to the dark samples indicates that photooxidized components of the Macondo crude oil become water-soluble after irradiation. The predominance of higher-order oxygen classes indicates that multiple photochemical pathways exist that result in oxidation of petroleum compounds. Previous studies looking at oil dissolved in DCM as a function of light exposure, show loss of fluorescence over time. Oil is composed of many polyaromatic hydrocarbons (PAHs), and as the fluorescence data suggests they began to photodegrade, we believe this accounts for the explosion of water-soluble compounds observed in the 12 h exposure times. As the exposure time increased, a decrease in the formation of water soluble compounds was observed for the $O_x$ species. For the NO$_x$ species, the distribution expanded, however the most abundant distributions (red) changed as a function of irradiation time. The expansion of the NO$_x$ compounds suggests that these WSO compounds are more stable. As more oxygens are added to each molecule, the oil compounds decompose and decrease in molecular weight. Additionally, the energy created
due to stirring and light exposure formed an emulsion or “chocolate mousse”. In our samples, we observed the formation of emulsion starting after 24 hours of exposure and increased to form a stable emulsion or mousse after 48 hours of irradiation. We observed the outer layer of mousse formation beginning after 24 hours and believe that by 48 hours we reached a stable mousse.

**Introduction**

Photooxidation of crude oil has been extensively studied in the past 25 years following the Exxon Valdez Oil spill.\(^2\)\(^{106-107, 129, 131, 133, 134, 146, 153, 157-161}\) Despite the many reports on photooxidation of petroleum\(^2\)\(^{106, 107, 131, 133, 161-164}\), there is still a need for understanding the basic photochemical processes that occur when petroleum is exposed to sunlight. Reactive transients play an important role in the basic processes that occur when sunlight interacts with spilled oil. Previous studies have reported on the formation of hydroxyl radical from thin oil films over water\(^2\)\(^{27}\). Sunlight exposed oil films produced \(~4 \times 10^{-7}\) moles of hydroxyl radical in 24 h from 100 mg oil films\(^2\)\(^{27}\). Steady state concentrations in 10 mL of water under these films were 1.2-2.4 \times 10^{-16} M during 3 hour irradiations\(^2\)\(^{27}\). The hydroxyl radical study demonstrated that the fate of oil and other dissolved species following oil spills is heavily dependent on the formation and reaction of hydroxyl radical\(^2\)\(^{27}\). Other studies have reported on the solar production of singlet oxygen from crude oil on water\(^7\)\(^{154, 165}\). The oil used in these studies were from different sources including Macondo well oil\(^154\). For thin Macondo well oil films (100 mg, 60 microns thick), the total amount of singlet oxygen produced in one hour irradiations over 10 mL of Gulf of Mexico water and pure water were 1.9 \pm 0.4 \times 10^{-5} and 1.6 \pm 0.3 \times 10^{-5} mol, respectively\(^154\). Steady state concentrations of photoproduced singlet oxygen were also determined and found to be near 1 \times 10^{-12} M in water under thin films of oil\(^154\), which is considerably greater than values previously observed for unpolluted freshwater and seawater\(^18, 32, 35\). The data from these studies measuring singlet oxygen and hydroxyl radical photoproduced from thin oil films illustrate that oil is a source of hydroxyl radical and singlet oxygen. These studies provide knowledge regarding pathways and mechanisms of oil degradation. In order to truly understand the fate of spilled oil, identification of photoproducts is important. *Deepwater Horizon* oil has been well characterized. The types of compounds that are in the oil are polyaromatic hydrocarbons, alkanes, to name a few. Since the DWH oil is
composed of many PAHs, and PAHs are chromophores, we believe these compounds are responsible for oil photochemistry and they become oxygenated as a result of exposure to sunlight. Once oxygenated, PAHs become water-soluble and can cause negative effects to the ecosystem.\textsuperscript{166-169} Another study focused on the production of water soluble organics (WSO) formed after solar irradiation of Macondo well oil on pure water\textsuperscript{153}. Fourier transform ion cyclotron mass spectrometry (FT-ICR MS) was used to catalogue molecular level transformations that occur to Macondo derived WSO after solar irradiation\textsuperscript{153}. The results from this study reported on the increased abundance of higher-order oxygen classes in the irradiated samples relative to the dark samples, indicating that photooxidized components of the Macondo crude oil become water-soluble after irradiation\textsuperscript{153}. The predominance of higher-order oxygen classes observed in this study demonstrated that multiple photochemical pathways exist that result in oxidation of petroleum compounds\textsuperscript{153}. There are many factors that can inhibit or slow down photochemical processes. The formation of water-in-oil emulsions or “chocolate mousse” has been reported to affect oil behavior, specifically biodegradation and photochemical oxidation.\textsuperscript{170} Thingstad \textit{et al} reported that photochemical oxidation and biodegradation of oil compounds are directly impacted by emulsion or “chocolate mousse” formation.\textsuperscript{170} The mousse formation creates a film which protects the bulk oil layer and shields it from microbes and due to its opaque nature, also shields it from light.\textsuperscript{170} Thingstad \textit{et al} also reported that the formation of “surface active” oil soluble compounds was caused by photochemical oxidation of oil components\textsuperscript{170}. Due to sea energy or mixing, these “surface active” oil soluble compounds retain water within the oil once a certain concentration is reached\textsuperscript{170}. Mackay \textit{et al} conducted a series of experiments on the mechanistic formation of oil-in-water emulsions.\textsuperscript{171} They concluded that the asphaltenic like compounds were responsible for the encapsulation of the water droplets which eventually form emulsions.\textsuperscript{171} According to Thingstad \textit{et al}, stable mousses form when the bulk of the oil mass is encapsulated within the oil which forms the outer layer of the mousse\textsuperscript{170}.

Oil spills occur all over the world and the next oil spill is imminent. Predicting the photochemical fate of oil solely due to photochemistry will provide a basis for understanding the processes and mechanisms that occur in oil when released into aquatic systems. The current study investigated these changes as a function of irradiation time in both Gulf water and pure
water systems. These results will provide information regarding the fate of oil after prolonged exposure to sunlight.

**Experimental Section**

Crude oil from the Macondo well (MC 252) (received from BP, August 2011, chain of custody number 20110803-Tarr-072) was placed in the amount of 10 mL over 100 mL of pure water or Gulf of Mexico (GW) water in a jacketed beaker and stirred in the dark for 7 days at 27 °C. After 7 days, the equilibrated sample was then exposed to simulated sunlight at 27 °C while stirring 12, 24, 48, and 120 h, which are equivalent to 3, 6, 12, and 30 days of average solar irradiation in the Northern Gulf of Mexico. Details for simulated sunlight are provided in Chapter 2. A dark control was prepared in the same manner, but not irradiated. Both dark and irradiated blank pure water and GW water samples (no oil) were prepared and analyzed in the same manner as other samples. After separating the oil and water, aqueous samples were then extracted to collect a base/neutral fraction and an acid fraction according to previously reported methods. Prior to FT-ICR mass analysis, a stock solution (1 mg/mL) was further diluted to yield a final concentration of 125-250 µg/mL in equal parts (vol:vol) toluene:methanol spiked with 1% NH₄OH (negative ESI). Ionization source conditions and detailed experimental conditions are detailed in the Appendix A4.

**Results and Discussion**

**DBE vs. Carbon Number images for O₅ Classes**

Figure 8.1 shows the combined isoabundance plots for DBE vs. carbon number for GW WSO acid fraction and NPW WSO acid fraction time series for the O₅ class analyzed by (-) ESI using FT-ICR MS.
**Figure 8.1.** Combined isoabundance plots for a) NPW b) GW time series analyzed by (-) ESI FT-ICR MS.

The O$_1$-O$_{10}$ classes were combined to observe global changes for each exposure time and water matrix. Images are shown for 12 h, 24 h, 48 h and 120 h irradiation times for the O$_x$ series. Figure 8.1a and 8.1b present the data for the NPW and GW results, respectively. The dark Macondo-derived water-soluble acids are on the left and irradiated acid fractions are on the right for each water matrix. Previous studies report on the increase in relative abundance of higher-order oxygen classes over time after 12 h of irradiation in NPW$^{152, 153}$. We see similar trends for the 24 h, 48 h and 120 h time series irradiated acid fractions. With increasing exposure time, there is a loss of DBE and carbon number. This can be observed by looking at the edge of the distribution at DBE 17 and C$_{30}$ in the GW 12 h sample and following the loss of this edge to 120 h. A contraction is observed as the irradiation time increases to 120 h. At
120 h, the edge of the distribution decreased to DBE 14 and C_{25}. Additionally, the red region, which represents to the most abundant compounds, shrinks with increasing exposure time. Several isoabundance plots were selected to show the dramatic changes in the DBE vs. carbon number plots as a function of increasing exposure time. The changes observed for each distribution were outlined along the outer edge of each time series isoabundance plot. These outlines are illustrated in Figure 8.2.

![Figure 8.2](image)

**Figure 8.2.** Outlined images for a) O_x b) O_2 and c) N_1O_x d) O_8 GW time series acid fractions analyzed by (-) ESI for 12 h (blue), 24 h (green), 48 h (red) and 120 h (purple) exposure times.

The 12 h (blue), 24 h (green), 48 h (red) and 120 h (purple) distributions show changes over time for each series. With the exception of the N_1O_x class, the distributions contracted as exposure time increased. The N_1O_x series expanded as exposure time increased which could suggest that the loss of the C_{3}H_{5}O_{x} compounds are increasing the abundance of the other heteroatom species. In the case with the oxygen classes, we theorize that as more oxygens are added, the oil compounds are decomposing. Previous studies looking at loss of fluorescence over time in the Macondo well oil layer, correlate with the decomposition of high molecular
weight (MW) species over time. King et al monitored the loss of fluorescence of oil as a function of irradiation time. The maximum fluorescence peak was measured as a proxy for the total PAH content for 60 µm Macondo Well oil films. Other reports studied the loss of fluorescence as a result of photodegradation of crude oil. The loss of higher molecular weight species over time was observed in DBE vs. carbon number plots for the WSO acid fraction analyzed by (-) ESI. The fluorescence results correlated with these findings. The longer exposure time show species decreasing in MW as the oxygen content increases. We infer that these compounds are breaking up into smaller compounds as they transition to complete mineralization into CO₂. Figures A2-A3 show the DBE vs. carbon number plots for O₁-O₁₀ series. This trend can be observed for each Oₓ class.

**DBE vs. Carbon Number images for N₁Oₓ Classes**

Figure 8.3a shows the DBE vs. carbon number images for NPW acid fraction and 8.3b shows GW acid fraction for the N₁Oₓ classes. The dark acid fractions are on the left and irradiated acid fractions are on the right.
Similar to the O$_x$ series, there is a loss of DBE and carbon number as irradiation time increases. Starting at 12 h (DBE 25, C$_{45}$), a contraction is observed in the distribution as irradiation time increases for the grey area. At 24 h (DBE 20, C$_{40}$), 48 h (DBE 20, C$_{35}$) and finally at 120 h, the distribution edge contracts to DBE 20, C$_{33}$. Furthermore, there is a noticeable shift in the most abundant compounds (red regions) starting at 12 h. Figure 8.3b, the red region is around DBE 12, C$_{20}$. At 48 hours, the red area begins to split and a second red region begins to appear around DBE 8, C$_{20}$. At 120 h, the red region that was observed around DBE 12 has completely shifted to around DBE 8. In contrary, the dark blue region shows an expansion in the

**Figure 8.3.** Combined isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for a) NPW b) GW N$_1$O$_x$ class without irradiation (left) and after irradiation (right).
distribution with increasing irradiation time (refer to figure 8.2). Again, we infer that as more oxygenation occurs, we observe decomposition of the compounds. Since the data is based on relative abundance, we believe the apparent increase observed for the \( \text{N}_1\text{O}_x \) compounds is directly related to the decomposition of the Ox species. Figures A35-A41 shows images for the \( \text{N}_1\text{O}_1\text{-N}_1\text{O}_8 \) individual isoabundance time series class plots.

**Van Krevelen Diagrams for Compound Class Comparison after Irradiation**

Van Krevelen plots provide a means to graphically interpret complex organic mixtures\(^4^9\). They project the elemental composition onto two axes according to the H/C and the O/C atomic ratios\(^4^9\). The H/C ratio distinguishes compounds based on their degree of unsaturation and the O/C ratio separates based on oxygen content present in the compound\(^4^9\). This manuscript utilizes van Krevelen diagrams to graphically distinguish dark and irradiated WSO acid fractions derived from negative-ion ESI using FT-ICR mass spectrometry. A difference plot highlights any compositional changes between dark and irradiated samples to show compounds that are unique to each fraction. Figure 8.4 shows the van Krevelen diagram for the \( \text{O}_1\text{-O}_{10} \) series in the negative-ion ESI acid fraction in GW for each exposure time.
Figure 8.4. van Krevelen plots for the DWH time series O\textsubscript{1}-O\textsubscript{10} classes of the acid fraction by (-) ESI in GW for a),d),g),j) dark sample, b),e),h),k) irradiated sample, and c),f),i),l) subtraction plot showing compounds unique to the dark or irradiated sample.
Each point on the plot represents a single sample or a distinct elemental composition. Figure 8.4a-b illustrates the 12 h, 8.4d-f the 24 h, 8.4g-i the 48 h and 8.4j-l the 120 h, acid fractions for the O$_1$-O$_{10}$ classes using negative-ion ESI. After 12 hours of exposure, the amount of water soluble aromatics increased shown by the density of yellow points (aromatics) and red points (condensed aromatics). The 12 h irradiated fraction (b) showed a more dense region in the yellow and red points which indicates increased oxygenation of these species as a result of solar exposure. As exposure time increased to 24 h, a shift to the right and a decrease in the number of aromatics (red and yellow points) was observed. This trend continues from the 24 h (e), 48 h (h) through the 120 h (k) and is most likely due to photodegradation of the aromatic compounds. Such photodegradation of the aromatic compounds has been previously reported by following the loss of fluorescence in the oil layer as a function of exposure time. The corresponding van Krevelen difference plots are represented in Figure 8.4c,f, i, l for increasing exposure time. The difference plots show that after irradiation many new compounds are formed (blue points), specifically compounds that show increased oxidation (shift to the right) and hydrogen deficiency (shift downward). Again, after 12 h of exposure (8.4c), many new oxygenated species are formed which can be seen between H/C 0.7-1.5 and O/C 0.1-0.3. As the exposure time increased from 24 h to 120 h, the population of blue points decreased, suggesting that the compounds were being photodegraded. The results from the 12 h GW study agrees with previously published results in NPW. A more detailed explanation of these findings has been published elsewhere. Figure 8.5 represents the van Krevelen plots for the time series GW WSO acid fraction for the N$_1$-N$_{10}$ classes. Similar to the oxygen classes, the same trends were observed. After exposure to light, an increase in the amount of oxygen was observed as well as the formation of many unique compounds (Figure 8.5 c,f,i,l blue points). The shift to the right is indicative of increased oxidation and has been previously reported for 12 h NPW studies. Figures A43-A44 show the van Krevelen diagrams for the NPW time series samples, showing the same trends.
Heteroatom Class Distribution as a Function of Irradiation Time

Heteroatom class distributions derived from negative-ion ESI FT-ICR MS comparing the relative abundances between irradiated and non-irradiated water soluble acidic species can easily illustrate universal changes between samples. Figure 8.6a compares the relative abundances between each exposure time for $O_1-O_{10}$ water soluble acidic species without irradiation in GW. Without irradiation, the $O_2$ class is the most abundant for all exposure times correlating well with previous results reported for 12 h exposure times\textsuperscript{153}. Figure 8.6b presents the results for the irradiated time series $O_1-O_{10}$ class in GW.

Figure 8.5. van Krevelen plots for the DWH time series $N_1-NO_8$ classes of the acid fraction by (-) ESI in GW for a),d),g),j) dark sample, b),e),h),k) irradiated sample, and c),f),i),l) subtraction plot showing compounds unique to the dark or irradiated sample.
After irradiation there is a shift in distribution to the right and higher-order oxygen classes (O₄-O₁₀) increase in abundance over time. From 12 to 24 hours, O₅-O₉ increased in relative abundance for the irradiated samples. Figure A43 compares the heteroatom class distributions for the irradiated and non-irradiated O₁-O₁₀ species in NPW. The same trends can be seen in the NPW as the GW. The increase in oxygens as a result from photochemical reactions has been reported elsewhere\textsuperscript{153}. The time series results provide evidence that over time, the number of oxygens per molecule increases, therefore the water solubility of oil-derived compounds increases. This result is in agreement with previous results reporting on enhanced

![Figure 8.6. Heteroatom class plots plots for the DWH time series O₁-O₁₀ classes of the acid fraction by (-) ESI in GW for a) dark sample, b) irradiated sample.](image)
water solubility as a result of photooxidation\textsuperscript{91,153}. However, this is the first report on enhanced oxidation as a function of exposure time. Figure 8.7 highlights N\textsubscript{1}O\textsubscript{x} classes detected in Gulf water soluble acidic fractions.

**Figure 8.7.** Heteroatom class plots plots for the DWH time series N\textsubscript{1}O\textsubscript{1}-N\textsubscript{1}O\textsubscript{10} classes of the acid fraction by (-) ESI in GW for a) dark sample, b) irradiated sample.

Without irradiation (8.7a), the N\textsubscript{1}O\textsubscript{3}-N\textsubscript{1}O\textsubscript{4} classes dominate in relative abundance in the GW WSO acidic fraction. After irradiation (8.7b), there is a shift to the right in the distribution from N\textsubscript{1}O\textsubscript{3}-N\textsubscript{1}O\textsubscript{10}. This result agrees with increased oxygenation after irradiation and has been previously reported for 12 h irradiations\textsuperscript{153}. Further explanation regarding these findings can be found elsewhere\textsuperscript{153}. For all exposure times, the N\textsubscript{1}O\textsubscript{5}-N\textsubscript{1}O\textsubscript{7} species increased in relative abundance over time. Figure A45 illustrates the heteroatom class distributions for the N\textsubscript{1}O\textsubscript{x}
time series performed in NPW. The same trends are observed for the NPW studies without irradiation, however, due to the polarity of seawater, more compounds were observed in the irradiated NPW than in the GW.

**Formation of Chocolate Mousse as a Function of Time**

The formation of oil-in-water emulsion or “chocolate mousse” was observed over time. Figure 8.8 presents an image of 12 h (3 day equivalent), 24 h (6 day equivalent), 48 h (12 day equivalent) and 120 h (30 day equivalent) exposures of Macondo well oil. A 120 h dark is compared as a control.

![Image of chocolate mousse formations at different times](image)

**Figure 8.8.** Shows changes to oil layer after exposure to light for 12, 24, 48 and 120 hours. A dark control is shown on the left for 120 h for comparison.
Formation of emulsion was apparent in the 3 day equivalent exposure and continued to increase with prolonged exposure. After 30 days of sunlight equivalent, a thick mousse was observed. It is inferred that at this time, the mousse is stable due and surrounds the bulk of the oil. According to Thingstad and Pengerud, the longer the mousse exists, the more stable it becomes.\textsuperscript{170} Since we began to observe its formation after 24 h of exposure, by 120 h (equivalent to 30 days of sunlight) the mousse is assumed to be stable.

**Conclusion**

Changes in WSO production were observed as a function of irradiation time in NPW and GW matrices at 12 h, 24 h, 48 h and 120 h. Investigation of the O\textsubscript{x} isoabundance plots concluded that the distributions for DBE vs. carbon number contracted as exposure time increased. This contraction is due to the photodegradation of the WSO species over time. For the N\textsubscript{1}O\textsubscript{x} class, the distributions became enlarged as exposure time increased. Since the isoabundance plots are based on relative abundance, this correlated with the loss of O\textsubscript{x} species over time. Once the O\textsubscript{x} classes are photodegraded, then an increase in the relative abundance for the other species present in the sample will be observed. The formation of chocolate mousse was observed starting at 24 hours and by 48 hours a stable emulsion was observed. The knowledge gained from this study suggests that the WSO products will continue to degrade as exposure time increases and eventually complete mineralization will occur. This study provides information regarding weathering conditions for spilled oil that are specifically due to photochemistry. Coupling this information to other weathering processes can provide data for oil spill modeling and improve our understanding regarding the photochemical fate of spilled oil in aquatic environments.

**Chapter 9. Future Work**

**Reactive Transients**

Future studies with DWH oil will utilize the methods for hydroxyl radical and singlet oxygen to measure steady state concentrations and total trapping to study the effect of dispersant.
Corexit 9500A and 9527 will be added to the oil and exposed to simulated sunlight. Steady state concentrations and total trapping for each reactive transient will be measured. Individual compounds will be dissolved in a hydrocarbon layer and exposed to simulated sunlight. Steady state concentrations and total trapping for hydroxyl radical and singlet oxygen will be determined. These analyses will allow identification and quantitation of each oil component and provide information for oil spill modeling.

**Polar Photoprodusts-Water Soluble Organics**

Photoprodust (WSO) production with the addition of a photocatalyst in the form of TiO₂ or Fe₂O₃ will be analyzed using FT-ICR MS. This study will focus on the role of photocatalysts in altering the photochemical mechanisms and products. In addition to the photocatalyst, the effect of dispersant will also be investigated.

**Oxygenated oil photoprodusts**

The presence of oxygenated compounds formed in the oil fraction as a function of exposure time will be investigated. Reddy *et al* at Woods Hole Oceanographic Institution are analyzing the DWH time series oil layer (pictured in figure 8.8) to observe changes in the formation of oxygenated species as a function of time. This data, coupled with the WSO data, may provide a bigger picture of the changes occurring to oil as a result of photodegradation. Reddy *et al* will be utilizing two dimensional gas chromatography with a flame ionization detector or GC/GC-FID (refer to Figure 9.1) along with TLC-FID in order to assess these changes. Two-dimensional GC FID uses two columns with different stationary phases in order to resolve complex mixtures.
The chromatogram shown in Figure 9.1 presents data from the 24 h dark and irradiated oil fraction. The 24 h dark sample (blue) shows the presence of volatile compounds in the range of 0-300 seconds. After light exposure, the red portion indicates the formation of new compounds, which have decreased volatility and varying ranges of polarity. The TLC-FID work currently being conducted will isolate each polar group and give a breakdown of the oxygenated compounds present in the oil fraction. These studies are ongoing and will not be included in this dissertation.

Changes to biomarkers in the DWH time series oil fractions (Refer back to chapter 8, Figure 8.8) were studied using GC-MS and GC-MS-MS. Biomarkers are a group of hydrocarbons found in petroleum that are specific to the organisms once living in the material.
They provide information about the origin and history of the petroleum and are resistant to chemical change. Ed Overton at Louisiana State University has studied and published many manuscripts on changes to these compounds using GC-MS and GC-MS-MS. This study will focus on changes to these biomarkers as a function of irradiation time. Figure 9.2 illustrates a representative spectrum of a 12 hour irradiated sample and the biomarkers found in these samples. The spectra from each time series will be analyzed and compared to a dark control.

Figure 9.2. Representative chromatogram for GC/GC-FID performed by Reddy et al on the 24 h dark (blue) and irradiated (red) oil layer. The ordinate axis represents the retention times for the compounds eluted from the polar column and the abscissa represents the retention times for the compounds eluted from the volatile column.

This research is ongoing and will not be included in this dissertation.
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Figure A1. Rate of benzoic acid reaction vs. concentration of benzoic acid. (a) oil on nanopure water pH 8; (b) oil with 3% TiO$_2$ on nanopure water pH 8.
A2. Chapter 3 Supplemental Information

Fabrication of TiO$_2$ Nanotubes

500 mg of TiO$_2$ nanopowder (Aldrich) was weighed and added to 10 mL of 10 mM NaOH$^{12}$. The suspension was stirred for about 10 minutes and transferred into a 23 mL Teflon lined stainless steel autoclave. The autoclave was placed in a 150°C oven for 24 hours. The autoclave was removed from the oven and allowed to cool to room temperature (~4 hours). The resulting TiO$_2$ suspension was then transferred into a 50 mL centrifuge tube and washed three times with nanopure water to remove any excess NaOH. Samples were then transferred into a 150 mL beaker and the pH was adjusted to 3.0 ± 0.4 using 1 M HCl. Once pH was established, the sample was mechanically stirred for 24 hours to exchange the Na$^+$ with H$^+$. Once the exchange process was complete, the sample was washed with 30 mL of water three times and then once with 5 mL of acetone. The amorphous TiO$_2$ nanotubes were then transferred into a petri dish, allowed to dry, and heated at 350°C for 75 minutes. After the annealing process, TiO$_2$ nanotubes were characterized using TEM (Figure A2-a) and XRD (Figure A2-b).

Figure A2: (a) TEM image of TiO$_2$ nanotubes; (b) XRD pattern for TiO$_2$ nanotubes.
A4. Chapter 6 Supplemental Information

FT-ICR Parameters

Electrospray Ionization (ESI) Source and 9.4 T Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS)

All the WSO of DWH, NPO, HFO #1, HFO #2 and VAN oils were analyzed with a custom-built FT-ICR mass spectrometer\(^{173}\) equipped with a 9.4 Tesla horizontal 220 mm bore diameter superconducting solenoid magnet operated at room temperature (Oxford Corp., Oxney Mead, U.K.) and a modular ICR data station (PREDATOR) facilitated instrument control, data acquisition and data analysis\(^ {174}\).

Sample solutions were infused via a microelectrospray source\(^{175, 176}\) (50 µm i.d. fused silica emitter) at 0.5 µL/min by a syringe pump. Conditions for negative ion formation were emitter voltage, -2.7 kV; heated metal capillary -250V and heated to 110 °C. Ions generated by the ESI source were transferred from atmospheric pressure to the first pumping stage of the

Figure A3: Overlay of HPLC chromatograms (UV abs at 254 nm) for NP water layer under oil after 24h irradiation with 9% TiO\(_2\) (red) vs 24h dark with 9% TiO\(_2\) (blue). The large peak at ~7.6 min is benzoic acid which was added as a scavenger for hydroxyl radical. The many new peaks are water-soluble oil photoproducts that were not observed for the dark sample. Irradiation without TiO\(_2\).
mass spectrometer through a home built dual ion funnel assembly, originally developed at Pacific Northwest National Laboratory\textsuperscript{177} \textsuperscript{178} to increase ion transmission efficiency. The dc voltages applied on funnel are -100 V and -70 V, and on funnel 2 are -40 V and -10 V. Positive ion formation occurred at the same conditions as for negative ions, but with positive values.

ICR time-domain transients were collected from a 7 segment open cylindrical cell with capacitively coupled excitation electrodes based on the Tolmachev configuration\textsuperscript{179} \textsuperscript{180}. Seventy five individual acquisitions of 5.6 – 6.1s transient for each WSO sample were averaged, Hanning apodized,\textsuperscript{181} and zero-filled once prior to fast Fourier transformation. Broadband phase correction\textsuperscript{182} was applied to all mass spectra to increase resolving power by a factor of up to 2 than the conventional magnitude-mode resolving power.

**Mass Calibration and Data Analysis**

ICR frequencies were converted to ion masses based on the quadrupolar trapping potential approximation.\textsuperscript{183} Each m/z spectrum was internally calibrated based on an abundant homologous alkylation series differing in mass by integer multiples of 14.01565 Da (mass of a CH\textsubscript{2} unit) confirmed by isotopic fine structure based on the “walking” calibration equation.\textsuperscript{184} Experimentally measured masses were converted from the International Union of Pure and Applied Chemistry (IUPAC) mass scale to the Kendrick mass scale to identify homologous series for each heteroatom class. Peak assignments were performed by Kendrick mass defect analysis as previously described.\textsuperscript{185} For each elemental composition, CcHhNnOoSs, the heteroatom class, type (double bond equivalents, DBE = number of rings plus double bonds involving carbon) and carbon number, c, were tabulated for subsequent generation of heteroatom class relative abundance distributions and graphical DBE vs. carbon number images.
Figure A5: Jacketed beaker used in this study. The 250 mL beaker was jacketed and connected to a water circulator running at a temperature of 27 °C. The inner diameter of the beaker was 8 cm. During irradiation, the beaker was covered with a piece of quartz glass to reduce evaporation. In this photograph, 100 mL of water is in the beaker, but no oil is present.
Figure A6. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O₁ class without irradiation (left) and after irradiation (right).
Figure A7. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O₂ class without irradiation (left) and after irradiation (right).
**Figure A8.** Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O₃ class without irradiation (left) and after irradiation (right).
Figure A9. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O₄ class without irradiation (left) and after irradiation (right).
**Figure A10.** Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O₅ class without irradiation (left) and after irradiation (right).
Figure A11. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O₆ class without irradiation (left) and after irradiation (right).
Figure A12. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O<sub>7</sub> class without irradiation (left) and after irradiation (right).
Figure A13. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O₈ class without irradiation (left) and after irradiation (right).
Figure A14. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O₉ class without irradiation (left) and after irradiation (right).
Figure A15. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O\textsubscript{10} class without irradiation (left) and after irradiation (right).
Figure A16. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the $N_1O_1$ class without irradiation (left) and after irradiation (right).
**Figure A17.** Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the N1O2 class without irradiation (left) and after irradiation (right).
Figure A18. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the \( \text{N}_1\text{O}_3 \) class without irradiation (left) and after irradiation (right).
**Figure A19.** Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the \( \text{N}_1\text{O}_4 \) class without irradiation (left) and after irradiation (right).
**Figure A20.** Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the N$_1$O$_5$ class without irradiation (left) and after irradiation (right).
**Figure A21.** Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the N$_1$O$_6$ class without irradiation (left) and after irradiation (right).
Figure A22. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the \( \text{N}_1\text{O}_7 \) class without irradiation (left) and after irradiation (right).
Figure A23. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the \( \text{N}_1\text{O}_8 \) class without irradiation (left) and after irradiation (right).
Figure A24. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O₁ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
Figure A25. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O₂ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
**Figure A26.** Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O₃ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
Figure A27. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O₄ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
Figure A28. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O₅ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
**Figure A29.** Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O$_6$ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
Figure A30. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the $O_7$ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
Figure A31. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O₈ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
Figure A32. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the O₉ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
Figure A33. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the $O_{10}$ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
**Figure A34.** Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the N$_2$O$_5$ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
Figure A35. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the N$_1$O$_2$ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
**Figure A36.** Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the N$_1$O$_3$ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
Figure A37. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the N$_1$O$_4$ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
Figure A38. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the N$_2$O$_5$ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
Figure A39. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the N$_1$O$_6$ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
Figure A40. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the N$_2$O$_7$ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
Figure A41. Isoabundance-contour plots of double bond equivalent (DBE) vs. carbon number for water-soluble acidic species derived from negative-ion ESI FT-ICR mass spectra for the N$_1$O$_8$ class without irradiation (left) and after irradiation (right) for a) NPW and b) GW.
Figure A42. van Krevelen plots for the DWH time series O$_1$-O$_{10}$ classes of the acid fraction by (-) ESI in NPW for a),d),g),j) dark sample, b),e),h),k) irradiated sample, and c),f),i),l) subtraction plot showing compounds unique to the dark or irradiated sample.
Figure A43. van Krevelen plots for the DWH time series N$_1$-N$_1$O$_8$ classes of the acid fraction by (-) ESI in NPW for a),d),g),j) dark sample, b),e),h),k) irradiated sample, and c),f),i),l) subtraction plot showing compounds unique to the dark or irradiated sample.
Figure A44. Heteroatom class plots for the DWH time series O₁-O₁₀ classes of the acid fraction by (-) ESI in NPW for a) dark sample, b) irradiated sample.
Figure A45. Heteroatom class plots for the DWH time series N_{1}O_{1}-N_{1}O_{10} classes of the acid fraction by (-) ESI in NPW for a) dark sample, b) irradiated sample.
Vita

The author was born in Largo, Florida. Phoebe Z. Ray worked as an associate chemist for a pharmaceutical production company for 4 years. She received her bachelors’ degree in chemistry from the University of South Florida in 2007. She joined the University of New Orleans College of Sciences graduate school to pursue a Ph.D in Chemistry. She joined Dr. Matthew Tarr’s group at the University of New Orleans in 2012 and received her Master’s degree in Chemistry in 2014.