Proceedings of The National Conference On Undergraduate Research (NCUR) 2014 University of Kentucky, Lexington, KY April 3-5, 2014

Spectral Fluorescence Characteristics of Commercially Available Hydrocarbon Sensors

Stephanie Jocis Marine and Environmental Science United States Coast Guard Academy New London, CT 06320 USA

Faculty Advisor: Dr. Anni Vuorenkoski Florida Atlantic University Harbor Branch Oceanographic Institute Fort Pierce, Florida 34946 USA

Abstract

Due to the risk of oil spills in the marine environment, the ability to detect and characterize spilled oil with spectral fingerprinting has major significance. The objective of this study was to evaluate the sensitivity of seven commercial off-the-shelf (COTS) *in-situ* hydrocarbon fluorometers to single hydrocarbon compounds and crude oil water accommodated fractions (WAF). A spectrometer and fluorometer were used to characterize the spectral properties of parent polycyclic aromatic hydrocarbons (PAHs) and their alkylated homologs. The sensors were tested for responses to parent PAH compounds and to crude oil WAF. Absorbance and excitation-emission spectra indicated spectral properties of parent and alkylated PAHs were very similar. The sensor results were compared to colored dissolved organic matter (CDOM) responses to distinguish sensor sensitivity between CDOM and oil, revealing significant differences in sensitivity and selectivity. These results are being applied to field data collected in the Gulf of Mexico by a Bluefin Spray Glider. This study was conducted during a summer internship at Harbor Branch Oceanographic Institute at Florida Atlantic University.

Keywords: Fluorescence, Oil, Sensor

1. Introduction

As a result of increased oil exploration and an increased risk of oil spills in the marine environment, the ability to detect and characterize spilled oil with spectral fingerprinting has major significance. The objectives of this research included: use spectroscopy and fluorescence to characterize and compare Polycyclic Aromatic Hydrocarbons (PAHs) and their alkylated homologs and to test the sensitivity of commercially available off-the-shelf (COTS) instruments with varying optical parameters to measure the fluorescence of single compound PAHs, North Sea Crude Water Accommodated Fraction, and North Sea Crude chemically dispersed solution.

In the United States, the major energy sources include petroleum (oil), natural gas, coal, nuclear, and renewable energy. Out of the five major energy sources, petroleum accounted for 36% of the primary energy use in 2011, the largest contributor to United States primary energy. Also, oil provides 93% of the energy used for transportation, displaying reliance of the United States on oil production.¹

Petroleum is derived from the Greek words *petro* meaning rock and *oleum* meaning oil.² These Greek roots are fitting because gas and oil are formed from source rocks. Gas and oil are formed from organic matter preserved within sedimentary rocks. In the earth's crust, the zone where oil is generated is between 7000 to 18,000 ft, called the oil window. Oil formation is dependent upon not only the time and temperature, but the time at which the source rock is exposed to each temperature as it is continually buried deeper beneath earth's crust.³

As the oil and gas form within the shale source rock, there is a large volume increase that places stress on the source rock and fractures the shale. The hydrocarbons escape upwards through the fractures. Gas and oil have a lower density than the water that also occurs in the pores of subsurface rocks, therefore the oil and gas migrate within the source rock.³

If there is no trap on the migration route, the gas and oil will flow out of the source rock onto the surface as a gas or oil seep.³ Natural oil seeps are used to identify potential petroleum reserves and contribute the highest amount of oil to the marine environment. According to the National Research Council (NCR) of the U.S. National Academy of Sciences, natural oil seeps account for 46% of the annual oil in the marine environment throughout the world's oceans.⁴ With the increase in off shore oil exploration and deep sea drilling, there has been an increased number of marine oil spills, such as Exxon Valdez and Deepwater Horizon. With the heightened concern of oil's effect on the marine environment, it is crucial to be able to decipher between oil slicks from natural seeps and oil spills.

In every crude oil, there are four types of hydrocarbon molecules: paraffin or alkane molecule, naphthene or cycloparaffin molecule, aromatic or benzene molecule, and asphaltic molecule. In crude oil, paraffins account for 30% weight, naphthenes for 49%, aromatics for 15%, and asphaltics account for 6% weight.²

From the four types of hydrocarbon molecules, aromatic or benzene molecules may be fused together to created polycyclic aromatic hydrocarbons (PAHs). Aromatic or benzene molecules in addition to PAHs are considered to be the most acutely toxic component of petroleum products. Also, PAHs have known chronic and carcinogenic effects. In the marine environment, very little information is available on the forms and fates of PAHs. During weathering, alkyl and chlorine groups may attach to the PAHs and change the fate and effects characteristics of the petroleum in the marine environment.⁵ Although there are hundreds of components in crude oil, PAHs were studied because they are considered one of the most hazardous compounds in oil spills. The three parent PAH compounds studied in this experiment: Naphthalene, Phenanthrene, and Fluorene are listed on the EPA's Priority Pollutants list.⁶

When oil is spilled into the marine environment, fish may intake these hazardous compounds and in turn pass these carcinogens onto humans. In addition, PAHs are used for identifying and classifying spilled oil, differentiating between sources of hydrocarbons in the environment, and providing information on the extent of oil weathering in the marine environment. Once oil hits the marine environment, immediately physical and chemical reactions begin to take place in a process known as weathering. The main factors in weathering include evaporation, physical dispersion, surface spreading, oxidation, biodegradation, dissolution, emulsification and sedimentation.¹²

In regards to the parent PAHs being tested, all three parent PAH compounds are considered to have low molecular weight. Compared to high-molecular-weight PAHs, low-molecular-weight PAHs are more soluble and less volatile, yielding a lower affinity for surfaces. In general, alkyl substitution in PAHs typically decreases water solubility. In addition, alkyl PAHs are more persistent and tend to bioaccumulate more than parent PAHs.⁵

Based upon the characteristics of parent and alkylated PAHs, these characteristics can be seen in data collected from the Deepwater Horizon spill by Diercks et al. (2010).⁷ With the results from Diercks et al. finding at Deepwater Horizon, it is important to note that Deepwater Horizon was a major human, environmental and economic disaster that began on April 20, 2010.⁸ The marine environment in the Gulf of Mexico was severely damaged from the explosion of the oil platform and the introduction of 4.9 million barrels of oil into the fragile ecosystem.¹⁰ In the Deepwater Horizon spill, it took 87 days to cap the well located 5,000 feet below the water's surface. In attempt to control the spread of the oil to the beaches and other fragile ecosystems, floating booms, chemical oil dispersants, and burning were used.⁹

Chemical dispersants are chemicals applied directly to an oil spill with specialized equipment mounted on an airplane, helicopter, or ship. Chemical dispersants are used to break up the oil into micron-sized droplets that mix into the water column. Since the oil droplets are smaller, bacteria and other micro-organisms can biodegrade the oil in the water column more quickly than breaking down an oil slick on the surface. The chemical oil dispersant used in response to the BP Deepwater Horizon oil spill was Corexit 9500A. The dispersant was used to prevent the oil from reaching the shore and protected marine environments near the coast.¹⁰

In order to collect data from the Deepwater Horizon spill, the Monterey Bay Aquarium Research Institute (MBARI) sent an autonomous underwater vehicle (AUV) in May 2010 to collect information on deep oil plumes. This AUV collected water samples at various depths and identified and linked a persistent deep water plume to its source as oil from the Deepwater Horizon Macondo well blowout.⁹ As shown in this example, AUVs can be extremely useful in collecting data for oil spills. In this experiment, seven hydrocarbon sensors were tested to determine the best sensors to be placed in the Bluefin Spray Glider AUV, as shown in Figure 5.¹¹ The Bluefin Spray Glider is a deep-diving, buoyancy-driven AUV. The spray can be deployed for up to six months and collects data profiles using a pumped, conductivity-temperature-depth (CTD) sensor and other instruments, such as hydrocarbon sensors.¹¹



Figure 1. Bluefin Spray Glider by Bluefine Robotics.¹¹

According to the EPA, the fluorometers allow scientists to determine the oil plume location and differentiate chemically dispersed oil from naturally dispersed oil. Fluorometers utilize the fluorescence characteristics of oil and dispersed oil. Fluorescence is defined as the absorption of light at a certain wavelength that induces the emission of light at a longer wavelength with lower energy. To measure hydrocarbon fluorescence, fluorometers expose a compound to a specific wavelength in the Ultraviolet (UV) light range, which excites the compounds electrons to a higher energy state. When the electron relaxes back down to its ground state, it emits light and fluoresces. The fluorometer measures the emitted light. The excitation emission spectrum generated by fluorometers can be used to identify certain compounds in oil and dispersant effectiveness.¹⁰

When measuring fluorescence in the water column, there is naturally occurring dissolved organic carbon (DOC) that fluoresces in the same spectrum as oil. Colored dissolved organic matter (CDOM) is the light absorbing fraction of DOC that could interfere with the absorption of light when detecting oil in water. As CDOM naturally occurs in both coastal and open ocean regions, this experiment took into account the possible overlap and interference of CDOM when detected by hydrocarbon sensors.¹³

In this experiment, seven sensors were used for hydrocarbon detection. These sensors include Chelsea UV AquaTracka, Chelsea UviLux, Turner C3-Crude Oil, Turner C3-Turbidity, Turner C3-Chlorophyll, Turner Cyclops 7-CDOM, and Turner Cyclops 7-Refined Oil.

2. Methodology

2.1 PAH And Alkylated PAH Sample Preparation And Absorbance And EEM Data Collection

In order to look at the similarities and differences between the parent PAH compounds and the alkylated PAH compounds, each compound was prepared to a standard concentration of 1.0 mg/L. Phenanthrene was the first parent PAH compound to be prepared.

Once the 4.0 mL cuvette was filled with 1.0 mg/L phenanthrene in ethanol solution, the absorption and transmission of the solution was determined by Ocean Optics DH-2000 Spectrometer with UV-Vis-NIR light source. The cuvette was placed in the FluoroMax-3 by Jobin Yvon Horiba fluorometer. Using the software FluorEssence V3.5, 3D Spectra was generated using Excitation range 200 to 400 nm, slit width 5 nm, Emission range 300 to 500 nm, slit width 5 nm, and mask 1st and 2nd order Rayleigh scattering. The Excitation and Emission (EEM) spectrum was saved.

Then, the EEM spectra data was imported into MATLAB R2012 Alpha. Within the m-file, the excitation and emission ranges for each of the seven sensors were included and overlaid on each EEM spectra. The five hydrocarbon sensor ranges overlaid included the Chelsea Aquatracka, Chelsea UviLux, Turner C3-Crude Oil, Turner Cyclops 7-CDOM, and Turner Cyclops 7-Refined Oil.

After the preparation of phenanthrene and obtaining the absorption, transmission, and EEM spectra for the various phenanthrene concentrations, the same procedures were followed for naphthalene and fluorene. Then, the alkylated PAH samples began to be prepared in the same method as the parent compounds. The alkylated PAH samples prepared included: 2,3-Dimethylnaphthalene, 2,3-Dimethylnaphthalene, 1-Methylfluorene, 1-Methylphenanthrene, 3,6-Dimethylphenanthrene, 1-Ethylnaphthalene, and 1,2-Dimethylnaphthalene.

For every compound prepared, the absorbance and transmission spectra were obtained and an EEM spectrum was generated in MATLAB with the overlaid sensor ranges. Once all of the samples were prepared and data was obtained, the EEM spectra for the parent PAH and alkylated PAHs were compared. For naphthalene, phenanthrene,

and fluorene, the alkylated PAH spectra were similar to the parent PAH spectrum. Since the EEM spectra were so similar, only the parent PAH compounds were tested with the hydrocarbon sensors.

2.2 Parent PAH Sensor Data Collection

For the next phase of the experiment, the sensors were set up to test sensor response to the various parent PAH compounds. The linearity of the sensor responses were verified using Naphthalenedisulfonic acid disodium salt hydrate (NDSA) and Carbazole, which were prepared to calibrate the Turner Cyclops 7 – Refined Oil and Aquatracka sensors, respectively. The results were compared to manufacturer standards. In order to determine all seven sensor responses to naphthalene, three sensors mounted in the 2 L beaker filled with 1 L MilliQ water with a stirrer bar on the stirrer. The Aquatracka and C3-Crude Oil sensors were connected to the flow system with 4 L MilliQ water. A new log was created for naphthalene and the base sensor readings were recorded. For naphthalene, 298.5 mg/L solution was used. The data was then imported into MATLAB and plotted. Using the plots of the sensor data, the sensor output in volts was determined for each addition. Using Excel, the sensor output was plotted vs. concentration added to ensure linearity between the added naphthalene and sensor response.

Next, the same set-up process was followed for phenanthrene then fluorene. For fluorene, the 1 mg/L solution was doubled with each addition. The volume of the addition as well as the sensor responses were recorded in the log. The data collected was then plotted in the same procedure as for naphthalene.

2.3 Oil And Water Sample Preparation And Sensor Data Collection

For the third phase of the experiment, various oil samples were prepared and sensor response was tested. Before any oil samples were tested, CDOM was collected from the Florida Atlantic University (FAU) Harbor Branch channel. The water was then filtered by a 1.2 μ m glass filter to only have CDOM. The CDOM measurements were significant because typically the hydrocarbon sensors have difficulty differentiating between CDOM and oil at the edge of oil slicks, as natural seawater fluoresces due to CDOM.¹³

Once the CDOM was tested, the oil samples were prepared and tested with the sensors. First, a North Sea Crude (NSC) oil water accommodated fraction (WAF) sample was prepared. Two liters of MilliQ deionized (DI) water and a stirrer bar were placed in an aspirator bottle. Approximately 2 mL of North Sea Crude oil was inserted in the aspirator bottle and settled on top of the water. The aspirator bottle was then plugged and the stirrer was placed set to 390 rpm. A 1.4 g/L concentration of NSC WAF was created by pipetting 2.8 g of oil into the aspirator bottle. By following CROSERF standard protocol the oil in water solution mixed for 12 to 18 hours. The stirrer was then turned off and the solution sat for four hours. Once the NSC WAF sample settled, the aspirator bottle was drained into two 500 mL capped flasks to minimize evaporation. The aspirator bottle was drained until just below the oil line to ensure no contamination of the samples. Only the water, with dissolved oil, was collected.

Once the sample was collected, very small amounts were added to the sensors in a similar method as the single compound PAHs. The Chelsea UviLux, Cyclops 7-CDOM, and Cyclops 7-Refined Oil sensors were all placed in a 2 L beaker filled with 1 L MilliQ DI water. A stirrer bar was placed in the beaker, which sat on top of a stirrer set to 4 rpm. The Chelsea Aquatracka and C3-Crude Oil sensors were set up in a system of 4 L of water. The sensor responses were logged manually in Excel and logged by the sensors. 4 mL of the solution was placed in a cuvette. Then, the absorbance, transmission, and EEM spectra were obtained. The sensor data was plotted in MATLAB. From the sensor plots, Excel graphs were made to look at the response and linearity of the sensors.

Next, a North Sea Crude chemically dispersed solution was formed using Corexit 9500A. This solution was formed in the exact same method as above; however, 480 μ L of Corexit 9500A dispersant was added onto of the 2.4 g of NSC oil added to the 2 L of water in the aspirator bottle. This solution was a 1.2 g/L oil in water solution with a 1:5 dispersant to oil ratio. Once again, the solution stirred at 390 rpm for 12 to 18 hours and sat for four hours. The sample was tested by the sensors and plotted in the same manner as for the NSC WAF.

3. Results

Once all of the single compound PAH and Alkylated PAH compounds were prepared, the absorption and transmission were determined. In Figure 2, the absorption spectra for phenanthrene and the alkylated PAHs 1-Methylphenanthrene and 3,6-Dimethylphenanthrene are shown.



Figure 2. Phenanthrene Absorbance Spectra for parent and alkylated PAHs.

Next, the cuvettes containing the parent PAHs and alkylated PAHs were placed in the fluorometer to obtain Excitation Emission (EEM) spectra. On each spectrum, the five boxes represent the detection ranges of the five sensors tested. Figure 3 displays the fluorescence results for Naphthalene.



Figure 3. Naphthalene Excitation Emission Spectra for parent and alkylated PAHs.

Next, the Parent PAHs were added in double concentrations to be detected by the sensors. The Chelsea UviLux, Cyclops-7 Refined Oil, and Cyclops-7 CDOM sensor results to 1.0 mg/L fluorine are displayed below in Figure 4.



Figure 4. MATLAB plot from sensor response to 1 mg/L Fluorene.

After importing and plotting the sensor data in MATLAB, as shown in Figure 4, concentration of fluorene added in mg/L was plotted versus the sensor output in volts.



Figure 5. UviLux sensor response to doubled 1.0 mg/L Fluorene additions.



Once all of the single compound parent PAHs were tested with the sensors, the sensor response to the oil samples was determined. First, the North Sea Crude (NSC) Water Accommodated Fraction (WAF) 1.4 g/L oil in DI water sample was tested. Figure 7 shows the sensor response from the Chelsea UviLux, Cyclops 7-CDOM, and Cyclops 7-Refined Oil. The Chelsea UviLux sensor has two means of recorded the sensor response. The DAQ Plotter records the sensor response in volts and the T-Plot records the sensor response in Digital Counts. Both records are shown in Figure 7 to compare the results of the two different methods of acquiring data and sensor output.



Figure 7. MATLAB plot from sensor response to 1.4 g/L North Sea Crude Oil Water Accommodated Fraction.

After importing and plotting the sensor data in MATLAB, as shown in Figure 7, concentration of NSC WAF added in mg/L was plotted versus the sensor output in volts. The concentration of NSC WAF added was plotted versus the UviLux sensor response recorded by the DAQ Plotter and T-Plot program, in Figures 8 and 9, respectively.



Figure 8. UviLux sensor response to 1.4 g/L NSC WAF from DAQ Plotter.

Figure 9. UviLux sensor response to 1.4 g/L NSC WAF from T-Plot.

In addition, the results of the Cyclops 7-Refined Oil and C3-Crude Oil Sensor are shown below in Figures 10 and 11, respectively.



response to 1.4 g/L NSC WAF.

Figure 11. C3 – Crude Oil Sensor response to 1.4 g/L NSC WAF.

Lastly, in looking at Figure 9, the Chelsea UviLux T-plot MATLAB sensor response reveals sensor response detected a very low concentration additions of 1.4 g/L North Sea Crude WAF oil in water solution. Before the gain on the sensor was changed, the UviLux sensor response at low concentrations was plotted in Figure 12.



Figure 12. UviLux sensor response to 1.4 g/L NSC WAF from T-Plot, Low Concentration.

For the last sample to be tested by the sensors, the North Sea Crude chemically dispersed 1.2 g/L oil in water solution was tested by the sensors. The Corexit 9500A to oil ratio was 1:5. The sensor response of the C3-Turbidity, C3-Crude Oil, C3-Chlorophyll, and Chelsea AquaTracka sensors from additions of 1.2 g/L NSC chemically dispersed oil in water solution are shown in Figure 13.



Figure 13. MATLAB plot from sensor response to 1.2 g/L North Sea Crude Oil Chemically Dispersed in DI Water.

After importing and plotting the sensor data in MATLAB, as shown in Figure 13, concentration of NSC chemically dispersed added in mg/L was plotted versus the sensor output in volts. The concentration of NSC chemically dispersed added was plotted versus the Cyclops-7 Refined Oil sensor response in Figure 14 and versus the UviLux sensor response from T-Plot in Figure 15.



Figure 14. Cyclops-7 Refined Oil sensor response to 1.2 g/L NSC Chemically Dispersed.

Figure 15. UviLux T-Plot sensor response to 1.2 g/L NSC Chemically Dispersed.

Lastly, Figure 16 displays the spectral comparison between CDOM, NSC WAF, and NSC Chemically Dispersed with the sensor overlays.



Figure 16. Spectral Comparison between CDOM, NSC WAF, and NSC Chemically Dispersed solutions.

4. Discussion

4.1 PAH and alkylated PAH results

Beginning with Figure 2, phenanthrene's absorbance spectrum displayed defined peaks at 250 nm, 275 nm, 280 nm, and 295 nm. In both alkylated PAHs, 1-Methylphenanthrene and 3,6-Dimethylphenanthrene, the defined peaks were consistent. On the other hand, the 1 mg/L phenanthrene absorbance spectrum clearly has the highest concentration, with absorbance reaching above 1.8 m⁻¹. As the concentration decreased, the resolution and clarity of the peaks also decreased, as seen with 1-Methylphenanthrene. It was concluded that phenanthrene alkylated PAHs have similar absorbance spectra, but display a lower concentration. Although results are not shown above, the research conducted found similar conclusions for the parent PAHs naphthalene and fluorene.

Once the absorption spectra were obtained, the EEM spectra for 1 mg/L naphthalene, 1-Ethylnaphthalene, and 1,2-Dimethylnaphthalene were all produced, as shown in Figure 3. In comparing the EEM spectra, the range of the Excitation and Emission are all very similar. The Excitation range was 240-320 nm, while the Emission range was 310-380 nm. An important result was that the fluorescence spectrum of the parent and alkylated PAHs were very similar. In detecting hydrocarbons with the fluorescence sensors, the EEM spectra in Figure 3 reveal that fresh and weathered oil have similar fluorescent fingerprints. Although the results are not displayed above, the EEMs for phenanthrene and fluorene also displayed similar spectra between the parent and alkylated PAH samples.

Now, moving onto the fluorometer sensor data, the MATLAB plots from the sensor response to 1 mg/L fluorene are shown in Figure 4. Both the Chelsea UviLux and Cyclops-7 Refined Oil fluorometers displayed extremely sensitive and strong responses to doubled 1 mg/L fluorene additions. For the Chelsea UviLux, the sensor saturated at 5 volts and the Cyclops 7-Refined Oil Sensor saturated at both x100 and x10 gain. The large drops in the Cyclops 7-Refined Oil plot show the change in gain. The gain was changed on the Cyclops 7-Refined Oil fluorometer twice during the experiment because the sensor response was so strong to 1 mg/L additions of fluorene.

Using the sensor responses in Figure 4, the sensor output versus doubled additions of 1 mg/L fluorene are displayed for the UviLux sensor in Figure 5 and for the Cyclops 7-Refined Oil sensor in Figure 6. Figure 5 reveals an extremely linear response for the UviLux sensor. In addition, the UviLux sensor was extremely sensitive to the first additions and reveals a linear response to even very small amounts of the low concentration compound. Also, the UviLux response to 1 mg/L fluorene was the first compound that saturated the UviLux sensor, revealing a strong response to this single compound PAH. In Figure 6, only the three changes from the x10 gain in Figure 4 are shown in the plot. From this gain, the sensor response is extremely linear. Similar plots were created for the results to all the sensors for both phenanthrene and naphthalene, but fluorene created the most sensitive and linear sensor results.

4.2 North Sea Crude Oil Water Accommodated Fraction Results

Next, the fluorometer response was tested for the 1.4 g/L North Sea Crude oil water accommodated fraction. The MATLAB sensor responses to doubled additions of 1.4 g/L NSC WAF for the Chelsea UviLux recorded with DAQ plotter, Chelsea UviLux recorded with T-Plot, Cyclops 7-CDOM and Cyclops 7-Refined Oil are shown in Figure 7. In comparing the graphs, the T-Plot shows a greater volume and more sensitive data response. For the first time, the Cyclops 7-CDOM sensor shows a response. In addition, the Cyclops 7-Refined Oil shows a very sensitive and linear response to the 1.4 g/L NSC WAF.

Using the MATLAB sensor response shown in Figure 7, the UviLux sensor response from DAQ plotter and T-Plot recordings are shown in Figures 8 and 9, respectively. In Figure 8, the UviLux displays a linear and sensitive response to 1.4 g/L NSC WAF. The UviLux sensor detects the oil at very low concentrations. In addition, the sensor only reached 0.7 volts, which shows that it can detect a large quantity of oil in the water without becoming saturated.

Surprisingly, the C3-Crude Oil sensor did not have a strong response to the 1.4 g/L NSC WAF. The response is only somewhat linear, as seen in Figure 11, and the sensor output only increased 12 digital counts, which is very small. From the sensor response shown in Figure 7, the Cyclops 7-Refined Oil fluorometer response to 1.4 g/L NSC WAF reveals a very sensitive and linear response (Fig. 10). It is observed that the UviLux, Cyclops 7-CDOM, AquaTracka, and Cyclops 7-Refined Oil fluorometers all show linear and high sensitivity to detecting small concentrations of oil in water.

Lastly, Figure 7 shows the MATLAB plot from the sensor response by the Chelsea UviLux sensor in T-Plot. In Figure 7, it is apparent that the T-Plot data recorded sensor response at very low concentrations. Figure 12 confirms the extremely linear, low concentration response of the UviLux sensor to 1.4 g/L NSC WAF oil in water solution, the ability to detect less than 0.05 mg/L additions. This important result reveals that the UviLux fluorometer is very sensitive to detecting oil in water; however, these results can only be seen with the T-Plot, not the DAQ Plotter data.

4.3 North Sea Crude Chemically Dispersed Results

After the North Sea Crude oil water accommodated fraction was tested, a North Sea Crude oil chemically dispersed sample was created using a 1:5 Corexit 9500A to oil ratio. Figure 13 displays the MATLAB plots of the sensor responses to 1.2 g/L North Sea Crude oil chemically dispersed from the C3-Crude Oil, C3-Turbidity, C3-Chlorophyll, and Chelsea AquaTracka sensors. The 1.2 g/L NSC chemically dispersed solution is the first compound/sample that generated a response in the turbidity and chlorophyll sensors. In all four sensor plots shown in Figure 13, a high sensitivity and linear response can be seen by all the sensors. For the Chelsea AquaTracka, very sensitive and clean detections can be seen a very low concentrations.

Using the MATLAB sensor responses, Figure 15 displays that the UviLux T-Plot detects linear sensor responses at low concentrations. Figure 14 shows the response for the Cyclops 7-Refined Oil sensor, which does not appear to be linear throughout the range of concentration. For both the UviLux and Cyclops 7-Refined Oil, Figures 14 and 15 reveal not quite linear responses to the 1.2 g/L NSC chemically dispersed solution.

Lastly, Figure 16 displays the spectral comparison between CDOM, NSC WAF, and NSC chemically dispersed and shows how each sample has a distinct spectral peak. However, there is significant overlap between the CDOM EEM and NSC Chemically Dispersed EEM, which is important to note when detecting oil in the marine environment.

As a result of the experiments, it can be concluded that the absorbance and Excitation Emission spectrum for each alkylated PAH is similar to the parent PAH spectrum. For both the Chelsea UviLux and Cyclops 7-Refined Oil sensors, the sensors had an extremely linear and sensitive response to 1 mg/L doubled additions of fluorene, while both sensors were much less sensitive to 29.9 mg/L naphthalene. For the oil in water solutions, the C3-Crude Oil sensor surprisingly did not have a strong response to the 1.4 g/L NSC WAF solution. On the other hand, the Chelsea AquaTracka showed a very linear response and high sensitivity to the 1.4 g/L NSC WAF oil in water additions. The AquaTracka did not saturate and revealed a large detection range for crude oil in water. In response to doubled additions of 1.4 g/L NSC WAF solution, the Chelsea UviLux, Cyclops 7-CDOM, AquaTracka, and Cyclops 7-Refined Oil sensors all revealed linear and high sensitivity to detecting small concentrations of oil in water. In comparing the Chelsea UviLux DAQ Plotter data and Chelsea UviLux T-Plot data in response to 1.4 g/L NSC WAF, it is clear that the UviLux fluorometer displays sensitive detection to small concentrations of oil in water; however, these results can only be seen with the T-Plot, not the DAQ Plotter data output. For the chemically dispersed oil in water solution, the UviLux T-Plot once again revealed that the T-Plot sensor output detected lower

concentrations of oil in water than the DAQ Plotter and provided higher resolution data. With similar results to the NSC WAF solution, the Chelsea AquaTracka revealed extremely linear, very sensitive and strong response to the 1.2 g/L NSC chemically dispersed solution. On the other hand, both the UviLux and Cyclops-7 Refined Oil fluorometers did not show linear responses to the 1.2 g/L NSC chemically dispersed solution. Chelsea Aquatracka or Turner Crude, Turbidity, or Chlorophyll sensors are recommended to be used in detecting chemically dispersed oil in the marine environment. Lastly, distinct spectral differences were seen between CDOM, NSC WAF, and NSC chemically dispersed fluorescence signals.

For future studies and analyses, the sensor response for each single compound parent PAH and oil samples should be compared on a relative scale. Mechanically dispersed and weathered oil samples should be prepared and tested by the sensors. The absorption, transmission, and EEM spectra for Corexit 9500A should be determined to compare properties to the chemically dispersed oil in water solution results. Lastly, field data will be collected to compare exsitu results to in-situ results, as a Bluefin spray glider is currently deployed in the Gulf of Mexico collecting fluorometer data.

5. Acknowledgements

The author wishes to express appreciation to the United States Coast Guard Academy, United States Coast Guard Academy Alumni Association, the Link Foundation, Florida Atlantic University Harbor Branch Oceanographic Institute, LCDR Royce James, Dr. Dennis Danisak, Bluefin Robotics and the Battelle Memorial Institute, Liquid Robotics, Chelsea Technologies Group, the Gale Foundation, Dr. Gero Nootz, Joe Brooker, and my mentors Dr. Anni Vuorenkoski, Dr. Fraser Dalgleish, and Dr. Bing Ouyang.

6. References

- 1. EIA, Energy In Brief, U.S. Energy Information Administration, (2012), http://www.eia.gov/energy_in_brief/article/major_energy_sources_and_users.cfm
- 2. Hyne, N. J., *Nontechnical Guide to Petroleum Geology, Exploration, Drilling, and Production*, 2nd ed.; PennWell Corporation: Tulsa, OK, (2001), 1:14.
- 3. Hyne, N. J. *Nontechnical Guide to Petroleum Geology, Exploration, Drilling, and Production*, 2nd ed.; PennWell Corporation: Tulsa, OK, (2001), 149:165.
- 4. GPA, Natural Sources of Marine Oil Pollution, Global Marine Oil Pollution Information Gateway, http://oils.gpa.unep.org/facts/natural-sources.htm
- Irwin, R.J., VanMouwerik, M., Stevens, L., Seese, M.D., and W. Basham, Environmental Contaminants Encyclopedia PAHs Entry. National Park Service, Water Resources Division, Fort Collins, CO, 1997, http://www.nature.nps.gov/hazardssafety/toxic/pahs.pdf
- 6. EPA, Priority Pollutants, United States Environmental Protection Agency, (2013), http://water.epa.gov/scitech/methods/cwa/pollutants.cfm
- Diercks, A., Highsmith, R.C., Asper, V.L, Joung, D., Zhou, Z., Guo, L., Shiller, A.M., Joye, S.B., Teske, A.P., Guinasso, N., Wade, T.L., and Lohrenz, S.E., Characterization of subsurface polycylic aromatic hydrocarbons at the Deepwater Horizon site, *Geophysical Research Letters*, 37, (2010): 6.
- 8. Drilling, N. C., *Deepwater: The Gulf Oil Disaster and the Future of Offshore Drilling. Report to the President*, National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling, (2011).
- 9. The Ocean Portal Team, Gulf Oil Spill, Smithsonian National Museum of Natural History, (2013), http://ocean.si.edu/gulf-oil-spill
- EPA, EPA Response to BP Spill in Gulf of Mexico: Questions and Answers on Dispersants. United States Environmental Protection Agency, (2013), http://www.epa.gov/bspill/dispersants-qanda.html#list
 Bluefin Robotics, Bluefin Spray Glider Product Sheet, (2011),
- Bluenn Robolics, Bluenn Spray Glider Froduct Sheet, (2011), http://www.bluefinrobotics.com/assets/Downloads/Bluefin-Spray-Glider-Product-Sheet.pdf
 ITOPF, The Weathering Process, The International Tanker Owners Pollution Federation Limited, (2013),
- 12. ITOPF, The Weathering Process, The International Tanker Owners Pollution Federation Limited, (2013), http://www.itopf.com/marine-spills/fate/weathering-process/
- 13. Rochelle-Newall, E.J. and T.R. Fisher, Chromophoric dissolved organic matter and dissolved organic carbon in Chesapeake Bay, *Marine Chemistry*, 77, (2002): 23-41.