

Establishing a Baseline of Water Quality along the Coast of Northeastern North Carolina in Response to the Deepwater Horizon Oil Spill

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Abstract- Deepwater Horizon was an ultra-deepwater, semi-submersible, offshore drilling oil rig used for oil exploration and production purposes. The oil rig was owned by Transocean and was under contract to British Petroleum (BP). On April 20, 2010, the Deepwater Horizon had a wellhead blowout which caused an oil spill in the Gulf of Mexico. This incident caused a total of eleven deaths and injured seventeen of the workers. The Deepwater Horizon blowout is the largest oil spill in U. S. history.

The Deepwater Horizon was located north of the Gulf Stream Loop Current which is a warm ocean current that begins its path within the Gulf of Mexico. The Loop Current flows northward between Cuba and the Yucatan Peninsula, eventually curving east and south along Florida's coast and exiting through the Straits of Florida. The Gulf Stream then follows the coastlines of the United States and Newfoundland before crossing the Atlantic Ocean. These currents have the potential to bring oil from this spill to the Outer Banks of North Carolina.

This project sought to establish a baseline on a range of data correlating to water composition along the Outer Banks of North Carolina from Ocracoke Inlet to Corolla with concentrated sampling from Ocracoke Inlet to Cape Hatteras. The spectral fluorescence data was the main indicator for the presence of crude oil. The data obtained predates any appearance of oil from the Deepwater Horizon oil spill on the outer banks of North Carolina. The compilation of data will allow researchers to analyze variations between the baseline and future data collected.

I. INTRODUCTION

The Deepwater Horizon was a floating semi-submersible Mobile Offshore Drilling Unit (MODU) situated around 40 miles off of the Louisiana coast in the Macondo Prospect oil field. Deepwater Horizon was built by Hyundai Heavy Industries in 2001 for \$560 million. The Transocean Corporation had the ownership rights to Deepwater Horizon though the oil rig was under lease to British Petroleum (BP) until September 2013.

On April 20th, 2010 an explosion occurred on the Deepwater Horizon resulting in the death of eleven workers and injuring seventeen others. Ninety-eight people managed to survive the oil spill without injury. At the time of the explosion Deepwater Horizon was drilling an exploratory oil well at approximately 18,360 feet below sea level. It is estimated that around two million gallons of oil at a rate of

16,000 gallons per day has been spilled into Gulf of Mexico since the oil spill began making this the worst oil spill in United States history. BP is currently attempting to drill two pressure relief wells to intersect the pathway of the original ruptured well reducing the pressure and allowing the well to be capped with cement. BP has forecast to have the well capped between July 20th - July 27th according to a July 8th Reuters news release.

II. DATA COLLECTION

A. Overview

The Outer Banks of North Carolina was the location for the collection of water samples. The reason the Outer Banks was chosen for this research is because the Loop Current in the Gulf of Mexico is in close proximity to the Deepwater Horizon oil well, which connects to the Gulf Stream, which runs along the coast and has the potential to carry the oil off the shores of the Outer Banks.

The water samples ranged from Ocracoke Village, which is the southern most accessible point for the water samples to Corolla, the northern most accessible point. The water samples were collected from the 7th thru the 18th of June at each site. Thirty samples were collected in total. Outside air temperature, water temperature, wind speed and the wind direction readings were the taken. The pressure readings for each site were obtained by using Weatherunderground.com, which stores historical meteorological data for a given region on an hourly basis. Weatherunderground.com was also used as a comparative tool to confirm wind speed and wind direction readings.

B. Methods and Materials

To collect the data we used a Meteos branded anemometer, which measured the wind speed at each location, it also measured the outside air temperature. To measure the water temperature, a mercury thermometer attached to 40ft cotton line was used. The water samples were collected using a 20 oz plastic bottle with a 40 ft cotton line. A weight was attached to the bottom of the line to sink the plastic bottle in order to collect the water sample. Once the samples were collected they were transferred to a tinted glass bottle and put on ice to preserve any organic substances that were already

present within the water sample. Panoramic and ground images were also taken for each location to give a visual representation and documentation of the sampling sites. Images of this equipment can be found in Figure 1.



Figure 1: (clockwise) Water collection tool, temperature gauge, Meteos anemometer, Sony A200 camera

C. Data Identification

Each water sample and collection site was labeled with the date, time, and Global Positioning (GPS) coordinates. The GPS coordinates were recorded using a Garmin GPSMAP 60CSx. The time date and GPS coordinates were recorded to keep the samples in order and so that they could be recorded into a Microsoft Excel sheet to be used as a reference for future research.

III. FLUORESCENCE TESTING

A. Overview

In fluorescence a beam of light is used to excite electrons present in certain compounds within the oil. This beam of light causes the excited electrons to emit a light of a lower energy. There are four important characteristics that are unique to fluorescence; it is the result of the absorption of light, it occurs only during absorption, it involves the emission of light, and an outside source of energy is required.

Crude oil is a fossil fuel and the liquid variant of petroleum. Crude oil is the product of various plants and animals that have been buried under our earth's surface for a very long time. Due to the enormous heat and pressure being placed upon them, they degraded into substances such as oil and gas (fossil fuels). Crude oil is a mixture of organic molecules known as hydrocarbons, a combination of hydrogen and carbon.

The term petroleum encompasses a wide variety of fossil fuels; the liquid (crude oil), gaseous (natural gas), and solid forms (coal). Each petroleum variety has a unique mix of molecules that define its physical and chemical properties. The color of crude oil can vary from being extremely opaque, such as dark brown or black, to being completely transparent. The color of the crude oil is determined by its geographic

location, composition of its hydrocarbon groups, and other compounds present within the oil.

Crude Oil is composed not only of hydrocarbons, but other types of atoms as well. The varying levels of these molecules help to shape the organic makeup of the crude oil.

B. Percentage of Elements Present in Crude Oil

Carbon 83% to 87%
 Hydrogen 10% to 14%
 Nitrogen 0.1% to 2%
 Oxygen 0.1% to 1.5%
 Sulfur 0.5% to 6%
 Metals < 0.1%

C. Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons (PAH's), are the most common types of hydrocarbons that are found within crude oil. PAH's occur not only in oil, but coal and tar deposits as well. These fuels can be either fossil fuels or biomass. The aromatic hydrocarbons within PAH's gives researchers the ability to detect PAH's in oil due to their highly fluorescent attributes.

Due to the recent and still ongoing Deepwater Horizon oil spill, crude oil samples have become essential in testing for water quality. This is due to the crude oils bio-fluorescent qualities, which can be attributed to PAH's. The process of testing for fluorescence is known as fluorescence spectroscopy tested using Fluorometers.

Oils are typically excited using ultraviolet wavelengths (300-400 nm) and fluoresce in the visible wavelength range from 400-600 nm. The composition of the hydrocarbon chain as well as the other compounds present will determine its fluorescent capabilities.

IV. FLUORESCENCE TESTING HARDWARE

A. USB4000

The Ocean Optics USB4000 takes the analog light rays being transmitted from the Fluorescence Flow Cell and converts them to a digital signal. This digital signal is then relayed to the Spectrasuite software program and visualized into a graph displaying wavelength and intensity.

B. Fluorescence Flow Cell

A fiber sends excitation energy through a fused silica window into a 2-mm inner-diameter sample compartment. Emitted energy is collected by a second fiber, oriented at 90° that connects to a spectrometer configured for fluorescence. As the samples passed through the Fluorescence Flow Cell, light was being projected onto the samples via Tungsten Halogen LS-1 light source. The light refracts off of the fused silica window, in doing so, it causes compounds present within the samples to fluoresce. After the samples pass through the inner compartment, they exit the Fluorescence Flow Cell via the output tubing. They are then transferred to the waste collection bottle.

C. Spectrasuite

A spectrum is a band of seven colors that is obtained after white light is split. The Spectrasuite software reads the data

that is transmitted from the USB4000 and produces a visualization of the digital light signal depending upon the wavelength and intensity of the light that was refracted in the Fluorescence Flow Cell.

D. Tungsten Halogen LS-1 Light Source

Within the visible light spectrum every color has a specific wavelength in which it can be seen. The Tungsten Halogen LS-1 light source transmits white light with a wavelength spectrum of 360-2500 nanometers. The wavelengths can be altered when a colored filter is used. The Tungsten Halogen LS-1 light source provided a light spectrum for the compounds present within the samples to pass through. If any of the samples contained fluorescent compounds, they would be visualized in the intensities and wavelengths of the Spectrasuite graphs.

An illustration of the test equipment configuration can be found in Appendix A.

V. FLUORESCENCE RESULTS

A. Testing Outcome

Initially, it was thought that everything was running as it should have been. This was until the resulting graphs were collected for all thirty samples saved in the PNG format, a loss-less format utilizing no compression. The graphs were then converted to overlays in Photoshop. Overlays were created by using the magic-wand tool in Photoshop to remove the background of each graph. This is when it was realized that the only visible difference in all of the graphs was the intensity level. All of the graphs had similar spectrum readings differing only in intensity. In testing the graphs, they were found to be inconsistent with what has been displayed in reference articles.

The purpose of this project was not to search for oil in the water, but rather to see if any of the thirty samples collected could provide any peaks to use as a reference for when and if oil begins to enter into the water. Since the research experiment was testing for fluorescence, peaks were not expected to be found in the de-ionized water. This is because our de-ionized water samples did not contain any compounds and molecules that would cause it to fluoresce.

If the samples had been correctly tested they would have differed greatly in wavelength, as well as intensity. These graphs were forwarded to Dr. Jinchun Yuan, who is an ocean marine biologist, hoping that he could provide some insight on what was being seen. He indicated that the de-ionized water should be tested as a comparison level. The de-ionized water produced a similar wave pattern indicating that the test had been inaccurate. To verify that his assumptions were correct, Dr. Yuan contacted Ocean Optics, which is the manufacturer of the fluorescence software and hardware that was used for the experiment.

Several troubleshooting experiments were performed to try and locate the source of the problem. Dr. Yuan requested that the LS-1 light source be turned off while running the experiment. The results were no peaks, which should have been the case. This test verified that the USB4000 was functioning properly.

In the second test, he suggested that the test be ran in scope and irradiance mode. Scope mode is what had been used previously. The irradiance mode tested for irradiated energies being emitted from the samples. The results were the same peaks that had been seen previously in the earlier samples. This test was done to verify that the Spectrasuite software was functioning properly.

In the final test, blue glass was inserted into the LS-1 light source. Blue glass was chosen as a means of testing a different wavelength spectrum. Once the blue glass was inserted, de-ionized water was pumped through the Fluorescence Flow Cell and the fluorescence reading was relayed to the USB4000. The resulting de-ionized water spectrum graph was the same as the sample graphs. It should be noted, that a sharp decline occurred in wavelength peak, but the intensity remained relatively the same. The wavelength change can be attributed to the blue glass wavelength spectrum.

B. Future Fluorescent Recommendations

Fluorescence is a main indicator of determining oil components in water samples and the origin of that oil. It is recommended that further contact with Ocean Optics be made to arrive at accurate fluorescence readings. Tests should also be completed to ensure the Fluorescence Flow Cell is functioning properly. In a correctly functioning Fluorescence Flow Cell, de-ionized water would flow completely through without providing a fluorescence reading.

VI. WATER QUALITY

A. Overview

Clean water is essential for the survival of all ecosystems. The plants and animals in rivers, lakes, and oceans react to chemical changes in the natural water quality of their habitat. The change in the composition of species like phytoplankton, algae and bottom dwelling organism may indicate changes in water quality caused by an increase in the concentration of chemical nutrients in an environment, organic pollution, hazardous substances or oil.

B. Conductivity

The conductivity of a water-based solution is measured based upon the inorganic material or dissolved solids present within it. The ratio of ions in the water like cations (positively charged ions) and anions (negatively charged ions) will determine how conductive a particular water solution is. The temperature of the water also attributes to the conductivity of a given water solution. In conductivity, the higher the water temperature, the more conducted the reverse. The reverse holds true for solutions with colder temperatures. Conductivity can be measured in micromhos per centimeter or microsiemens per centimeter. The reason for testing the conductivity of the water samples is because organic compounds such as oil and alcohol do not conduct electrical current very well and therefore have a low conductivity when in water. To test for conductivity, a Hanna instruments designed DiST WP meter was inserted into the samples. It tests for conductivity by sending a charge through one probe and collecting it through the other probe. The speed of the

charge was indicative of the amount of organic materials or dissolved solids present within the samples.

C. pH

pH is the measure of acidity and alkalinity of a solution. The pH reflects concentration of hydroxide ions and hydrogen ions in given solution. High concentration of negatively charged hydroxide ions would result in a high pH. Low concentrations of negatively charged ions would result in a low pH, which would indicate a high concentration of Hydrogen ions. The pH scale goes 0-14 on a negative logarithmic scale with 0 being the most acidic and 14 being the most basic. The chemical and biological interactions affiliated with aquatic environments are greatly affected by pH. To test the pH a pH testing kit was used to perform the test each of the samples was poured into a separate Styrofoam cup. Once the samples were poured, the strip was inserted for a second and then removed and set on a level surface for 45 seconds. The strip was sat on a level surface so that it could dry and obtain an accurate reading. Once the strip set for 45 seconds the strip is then compared to the color chart that is provided on the bottle.

D. Salinity

Salinity is defined as the amount of dissolved salt in a particular body of water. This is typically measured in grams of salt per kilogram of water, expressed as a measurement of parts of salt per thousand parts of water (ppt). The salinity of the surrounding environment is an important constraint with which marine organisms must deal with, in order to survive. Diffusion refers to the “desire” of all matter to be equally concentrated in its environment. If a large concentration of something is put into a particular region of the environment, it will disperse until its concentration is uniform throughout the environment, provided it does not encounter any barriers through which it cannot pass. Salt exists in water as sodium ions (Na⁺) and chloride ions (Cl⁻). Charged ions like sodium ions and chloride ions are unable to pass through most biological membranes. However, water molecules are able to pass through most biological membranes, so salinity imbalances within biological systems are naturally corrected via the diffusion of water across biological membranes to equalize salt concentrations on both sides of the membrane. This process is known as osmosis, which is water diffusion through permeable membranes. The salinity levels in the samples were tested by using Aquacheck testing strips, which test the ranges of salinity from 400-7,000 parts per million (ppm) (mg/l). To perform the test, one inch of water from a sample was poured into a styrofoam cup. The Aqua check testing strip was then inserted into the water. After six minutes the yellow band at the top of the testing strip turned black, which indicated the test was complete and the results could be read using the chart provided on the Aquacheck bottle.

E. Results

The tests run for this project did not result in any unexpected readings. Salinity was high in the sounds due to extreme heating of the water over an extended period of time. The pH levels centered around 7.2-8.4. Conductivity tests

showed high levels of dissolved matter in the samples. Refined oil was added to a sample to illustrate that the conductivity readings drop considerably in the presence of oil. The test results did not show any substantial differences in the readings from the sound to the ocean.

VII. VISUALIZATION

Once the data was gathered and tests were completed, the results were gathered into visualization pages to be viewed by other researchers and scientists. This visualization utilized a combination of Google Maps, Adobe Photoshop, and scripting languages to present images and data in a geographic format. This allows the user to select the region of the Outer Banks that data was gathered for. A single view of the map can be found in Figure 2.

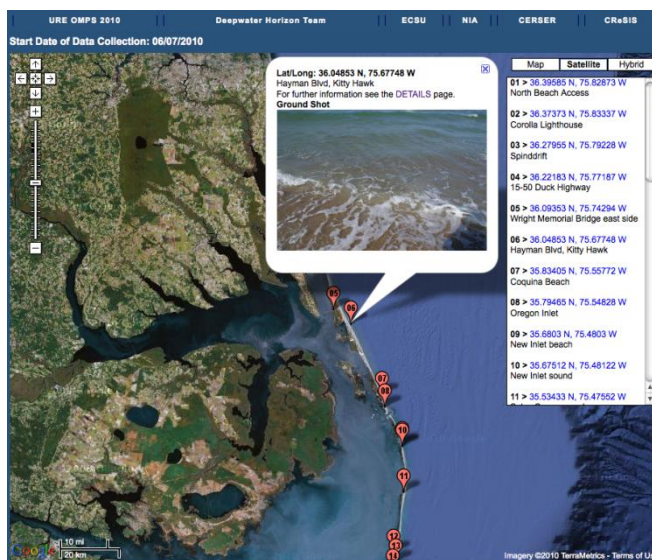


Figure 2: Google Maps Visualization

VIII. GOOGLE MAPS

A. Overview

Google Maps is a free web mapping application that is provided by Google. My Maps is a new feature, which allows users to create their own map by positioning markers onto a map. These maps can include street level view, satellite view or just the map itself. Google Maps also allows users to embed maps onto third party websites. The Deepwater Horizon team used Adobe Dreamweaver to complete our Google Map. Adobe Dreamweaver is a web development application that empowers designers and developers to build standards-based websites with PHP-based content management systems using JavaScript.

B. Markers

The Google Marker allows you to add and label sites inside of your Google Map. Google Marker is created using JavaScript code. JavaScript allows the team to create a function, which passed the latitude and longitude as parameters. Then, the function called the folder that holds the numbered markers graphics and displays them on the map.

The numbered marker allows the user to match the information in the sidebar to the marker on the graph. The

marker numbers are graphics stored inside a folder. Using JavaScript, the image is called inside a function to display the marker on the map.

C. Sidebar

The sidebar is located on the right side of the graph. This panel allows you to view the latitude, longitude and description of each location. It also allows you to click on the link to show the information window for that specific marker.

The latitude and longitude is an exact position of each location that a sample was taken from. It is also directly correlated to the latitudes and longitudes of the map.

The numbers in the sidebar match the numbers on the markers. JavaScript code was used to display the numbers inside of the sidebar application. JavaScript is a simple programming language used to make web pages more interactive and allows access to objects within a host environment. The host environment allows multiple modality components to share data, and coordinates the activities such as activation, deactivation, displaying and prompting.

The description gives the proper name of the location or nearby landmarks. From the description and latitude/longitude, it can be determined whether the water sample was collected from a sound or the ocean.

D. Information Window

The information window displays the latitude, longitude, description, link to the details page and ground shot thumbnail of each location. The following is displayed in the information windows:

1. The latitude and longitude directly correlated to the latitudes and longitudes in the sidebar of the map
2. Description of site
3. Link to Details Page for each collection site
4. The pH, conductivity and salinity of each location
5. A Ground Shot Thumbnail that allows the user to view a reduced size version of the actually image taken at the site.

E. Panorama

A panorama is a view of a physical space or three-dimensional model. A panorama was used to display a 360 view of each location. The panorama, coupled with the ground shots, gives a physical view of the water and the associated shoreline. An example of a panorama is found in figure 3.



Figure 3, Panorama in final format

Adobe Photoshop was used to stitch multiple photographs together to produce the panoramic view of the collection sites. Adobe Photoshop is a software program used for editing, creating, and modifying graphics for the web. The procedure for creating the panoramas is as follows:

1. Open Adobe Photoshop
2. Go to files and select “Automate”

3. Select “Photomerge” and select the images required to create the panorama
6. Once the images are selected, Photoshop will begin the attempt to generate the panorama

F. Displaying the Panorama

The Hypertext Markup Language (HTML) “<iframe>” tag is used display an inline frame. The HTML iframe tag allows the programmer to embed the panorama file within the current HTML file. The tag is inserted inside a table and is rendered as a window containing the panorama.

G. Details Page

The details page includes the latitude, longitude and proper description of each location. The user can also find ground shots images of each location. A panoramic view of the location and a graph that display the intensity of wavelength of the water sample is also available. The following items are displayed on the details page:

- Latitude/Longitude - The latitude and longitude is an exact position of each location that were visited.
- Description - The description gives you mental image of the location. From the description, you can tell whether the water sample was collected from the sound or ocean.
- Ground Shot - The goal of the ground shot was to show that there was no oil visibly present in the water.
- Panorama - The panoramic view was to show the user a 360° view of the location.
- Water Tests - The water tests show conductivity, pH, and salinity of each water sample.
- Intensity and Wavelength - This graph showed the intensity versus wavelength for each water sample.

H. Future Work

To display data in future projects it is recommended that a comma separated value (csv) file be used to be read by PHP coding. PHP is an open source scripting language that is suited for web development and can be embedded into HTML. The PHP script parses the CSV files into multiple variables and creates JavaScript code that Google Maps can utilize.

To establish a stronger baseline, the sedimentary layers, as well as, the organisms and microorganisms present in the sample locations should also be tested.

IX. CONCLUSION

Establishing scientific baselines in the face of impending changes in the environment is essential to the further monitoring, research, and recommendation of changes that can be made. This project established procedures, sites, and further tests that should be implemented in the eco-systems that make up the Outer Banks of North Carolina. While some tests did fail, the failures brought out the need for more communication with manufacturers and scientists. The lack of test equipment for more thorough water tests has prompted local managers to take stock of their equipment and the continuing need to keep it in good operating order. These

steps will lead to greater success for future researchers continuing this project.

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Appendix A: Fluorescence Testing Equipment Set-up

