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An Assessment of Fluorometric Techniques for Tracking the Transport of Polycyclic Aromatic Hydrocarbons from Groundwater into Surface Water Bodies

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AN ASSESSMENT OF FLUOROMETRIC TECHNIQUES FOR TRACKING THE
TRANSPORT OF POLYCYCLIC AROMATIC HYDROCARBONS FROM
GROUNDWATER INTO SURFACE WATER BODIES

by

Kyyas Seyitmuhammedov

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By

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APPROVED:

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ABSTRACT

A number of fluorometric techniques have been applied to characterize contamination associated with oil discharges and spills in the environment. While these techniques provide quick and lower cost alternatives to the many of the advanced techniques for characterizing oil-related constituents, their applicability still isn’t fully understood.

The objectives of this research were to understand the characteristics of organic transport in a linked surface-water/ground-water system, and develop some practical approaches using fluorometry to characterize the pathways of organic transport. The approach included modeling, field sampling and comparisons of laboratory analyses to assess basic field fluorometry techniques for characterizing sources and distributions of polycyclic aromatic hydrocarbons (PAHs) associated with oil discharges. The primary field site included a canal and nearby river, which resulted in generally uniform hydraulic gradient, such that petroleum and PAH contamination at the site could be characterized. Historical data provided general information on the distribution of contamination. Modeling using the Modflow groundwater flow package provided basic information on groundwater flow pathways and rates. Samples were collected from the canal, groundwater, the river and a treatment facility. Additional samples were collected from Bayou Corne sinkhole in Louisiana and the Deepwater Horizon crude oil spill in the Gulf of Mexico. The samples were analyzed for fluorometric absorbance using a 10AU field fluorometer, a Shimadzu absorbance spectrometer and a LS5 luminescence spectrometer (which provided fluorescence over a spectrum of frequencies). Additional analyses were completed using a gas chromatograph with a flame ionization detector (GC-FID) to provide a more complete qualitative description of the oil composition.

Analysis of the results from the 10-AU field fluorometer confirmed the capability of the field fluorometer to detect organic contamination resulting from crude and refined oil spills. Absorbance spectrometer results demonstrated possibility of using the PAH absorbance spectra to distinguish between the different types of oil, although more detailed analyses using various types of oil is recommended. The results using the luminescence spectrometer were consistent with GC FID results, and provided useful comparisons indicating the characteristics of fresh and weathered oil. The comparisons provide insight into the applicability of fluorometric approaches for characterizing transport pathways and concentrations of organic constituents associated with discharges of oil and other PAHs.
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1. INTRODUCTION

1.1. Background/Motivation

Tracking the source of organic contaminants is important for understanding the cause and potential solutions for many types of organic contamination problems in groundwater. The primary sources of organic contamination problems in groundwater are oil spills occurring by accidental or intentional releases. Oil spills discharge an average of 300,000 tons of oil per year is into the environment worldwide (Schmidt-Etkin, 2011). These spills occur both onshore or offshore depending on the location, sources, and activities leading to the oil spill. Schmidt-Etkin (2011) estimates that the highest contributors of oil spill types in United States are associated with spills during transportation of oil by vehicles or vessels, spills from inland pipelines, and spills from storage and consumption of oil and their products. Source tracking is necessary to determine the sources and types of oil associated with these spills.

Unfortunately, complete characterization of the sources of the organic constituents is often complex, time consuming, and costly. The widely used method for characterization of oil involves extracting it from the dissolved matrices, fractionating it to its compounds and analyzing it using gas chromatography techniques. Gas chromatography requires special attention to sample preparation, which requires time and effort depending on the complexity of the desired compound. Because of the difficulty in analyzing the organic constituents in these oil spills, effective remediation plans can be delayed and the regions of groundwater contamination can increase in size. Therefore, practical techniques are needed that can provide a reasonable characterization of the transport pathways and, to the greatest extent feasible, the sources.

A number of fluorometric techniques have been developed to characterize organic constituents. Researchers have been able to use fluorometric techniques to differentiate between different oil types depending on the specific density and in some cases depending on the amount of PAHs found in oil (Thruston and Knight, 1971; Ryder et al., 2002). The fluorometric techniques do not require the preparation of the sample for the analysis and can be performed on the field. Unfortunately, the factors that affect the application of these techniques are not well understood and the full potential for using these techniques is not fully known.
1.2. Goal and Hypothesis

The goal of this thesis is to assess the effectiveness of fluorometric techniques in characterizing the transport of polycyclic aromatic compounds associated with petroleum hydrocarbons in the environment. The hypothesis is that the use of a fluorometric techniques can serve as a useful tool in identifying the source of oil leading to PAH contamination in wells located downstream of the source. The scope concentrates on the detection and characterization of polycyclic aromatic hydrocarbons (PAHs) in groundwater. By applying fluorometric techniques to a sample collected from sites (or sources) that are relatively well characterized, this research will give insight on effectiveness of the fluorometric techniques and will provide recommendations for future research.

1.3. Overall Approach

The overall approach included sample collection and laboratory analyses, and comparison of the results using different analysis techniques to characterize a set of oil-contaminated samples obtained from different field sites. The primary field site is located in at a former mill in Massachusetts where groundwater has been contaminated by previous discharges of petroleum, chlorinated volatile organic compounds, asbestos, and heavy metals. The site configuration, which includes a canal and nearby river, resulted in a generally uniform hydraulic gradient between the two water bodies, such that PAH contamination entering the groundwater from the canal could be well characterized. Historical data provided general information on the distribution of contamination. Modeling using the Visual Modflow Flex 2014 provided basic information on groundwater flow pathways and rates. Samples were collected from the canal, groundwater, the river and a small treatment facility located at the site. Additional samples were collected from a sinkhole in Louisiana and the crude oil associated with the Deepwater Horizon spill in the Gulf of Mexico. The samples were analyzed for fluorometric absorbance using a 10AU field fluorometer, a Shimadzu absorbance spectrometer and a LS5 luminescence spectrometer (which provided fluorescence over a spectrum of frequencies). Additional analyses were completed using a gas chromatograph with a flame ionization detector (GC-FID) to provide a more complete qualitative description of the oil composition. The comparisons between the various analysis techniques provide insight into the applicability of fluorometric approaches for
characterizing transport pathways and concentrations of organic constituents associated with discharges of oil and other PAHs.

In this thesis, background information on oil chemistry and its physical properties affecting its transport in the environment is included in Chapter 2. In addition, Chapter 2 explains several of the fluorometric techniques that have been successfully used in previous research to distinguish oil types as well as ratios of oil compounds that have been used to differentiate the oil sources used in gas chromatographic techniques. Chapter 3 explains the methods and procedures of the techniques used to analyze oil in this research and Chapter 4 presents the results from the methods and their interpretation. Chapter 5 summarizes the conclusions developed from the results and provides recommendations for future work.
2. BACKGROUND

Characterization of oil-contaminated sites is often difficult given the complex characteristics and variety of constituents contained within oils. A variety of techniques have been developed to quantify the oils, their constituents, and their properties. This chapter provides some background information on the general characteristics of oils and the techniques used to quantify the nature and associated constituents contained in oils. Specific topics include general characteristics and physical and chemical characteristics and constituents in oil, the effects of weathering, gas chromatography techniques, and absorbance and fluorescence spectrophotometry for detection of oil contamination. The chapter concludes with brief description of the sample sites and field sites characterized in this research.

2.1. Oil Spills - Some General Characteristics and Factors

The occurrence of oil spills is common at offshore and onshore sites throughout the world. Offshore spills results from cargo ship activities and accidents (e.g. the Exxon Valdez and Deepwater Horizon Oil Spill) and onshore spills result from drilling activities and leaking from underground storage tanks. Depending where the oil spills occur, contaminants behave differently. For example, offshore spills are often transported great distances due to waves and currents. Onshore spills occurring on soil often enter the groundwater and often require longer time scales to reach surface water bodies. The characteristics of the oil and the specific spill location have an important effect on the transport of the oil constituents from these spills.

In addition to the site characteristics of the spill location, another important factor that effects transport of oil in the environment is the oil’s physical and chemical characteristics. Oils are complex compounds, consisting of many organic chemical compounds each affecting oils’ properties and behavior. Oils in the environment are often classified in two categories: crude oils and refined oils. A crude oil is oil that has not experienced any physical or chemical alteration and it is in its purest form, such as oil as found in soil formation below the ground. Refined oil is oil that has been altered by physical and chemical processes to create a product that is used on a daily basis (e.g. gasoline, diesel, Bunker C, etc.).
2.2. Chemical Composition of Oil

Depending on the chemical and physical properties, oils will behave differently in the environment. Therefore, an understanding of chemical and physical properties of the oil is important. Oils normally consist of a mixture of compounds that affect the properties and behavior of the oil during an oil spill. These compounds are divided into the following groups: saturates (alkanes), alkenes, aromatics and polar compounds.

Saturates (alkanes) typically comprise the larger portion of the compounds in oil mixture, such that they are often found in higher concentrations in the environments of areas affected by oil spills. Depending on the concentration ratios of the specific alkanes, the ratios of the compounds can be used to determine the origin of an oil spill. Another aspect of alkanes in determining the origin of the oil spill is that refined oils have different carbon numbered alkanes in them e.g. heavy fuel oils have high concentration of higher carbon numbered alkanes. (Wang et al. 2006)

Alkenes are products of cracking processes from larger molecules and are found only in some refined oil products (Wang et al. 2006). Thus, alkenes can be used as distinguishing markers between oil spills.

Aromatic hydrocarbons are found in all oil products, although the concentrations of aromatics are typically lower than the concentrations of alkanes. Aromatics are divided into two groups depending on the ring numbers. Aromatics with one ring are called BTEX and aromatics with two or more rings are called polycyclic aromatic hydrocarbons (PAHs) (Wang et al. 2006).

Polar compounds bond with nitrogen, oxygen or sulfur, which makes them to have positive and negative charges in their molecular structure (Wang et al. 2006). These compounds are generally found in lower concentrations in crude oil. However, heavy oils can have higher concentrations of polar compounds since their concentrations tend to increase with weathering (Wang et al. 2006). Thus, the presence of polar compounds with nitrogen, oxygen or sulfur has been used to predict extent of weathering and distinguish between oil products.

2.3. Physical Properties of Oil

The physical properties of oils are often as important the chemical properties since they are often correlated closely with the chemical properties. As such, an understanding of physical properties
of the oil is important to understand the transport behavior of oil in the environment. These properties of interest include density, specific gravity, solubility, viscosity, flash point, carbon distribution, distillation, and interfacial tension (Wang et al. 2006).

Density is the mass per unit volume. It shows if oil will rise or sink in the water (e.g. Bunker C will sink in the water). In addition, it is used to define oil as light or heavy crude oil (Wang et al. 2006).

Specific gravity is the oil’s density compared to the density of water at 15 Cº (Wang et al. 2006). This parameter is used by American Petroleum Institute (API) to define the density of oil:

\[
\text{API gravity} = \left[ \frac{141.5}{\text{density at } 15.6 \, \text{C}^\circ} \right] - 131.5 \quad \text{(Wang et al. 2006)}
\]

As the density of the oil decreases, the value of API increases (e.g. light oil has API gravity in the range between 35 and 45º API) (Wang et al. 2006). The solubility indicates the degree to which oil will dissolve in water. As the polarity increases, the solubility typically increases as well. Larger molecules also have lower solubility. Since oil is a complex compound, the solubility of oil in water is low. Nevertheless, even slightly dissolved concentrations of oil can be acutely toxic (Wang et al. 2006). Finally, it is recognized that interfacial tension can impact oil transport. Interfacial tension is the force of attraction and repulsion between the surface molecules of two different substances. The tendency of an oil to displace another fluid (or be displaced by another fluid) is affected by the interfacial tension. The interfacial tension and viscosity affect the extent oil will disperse on water (Wang et al. 2006).

2.4. Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds with two or more fused aromatic rings. In the environment, abundant PAHs have two (naphthalene) to seven (coronene) rings of fused benzene. Most PAHs consist of hydrogen and carbon atoms except for polycyclic aromatic compounds (PACs) for which nitrogen, oxygen, or sulfur replaces one of the carbon atoms. Other types of PAHs found in the environment include alkylated or branched PAHs in which an alkylated chain is attached to the ring (Boehm, 2006).

The sources of PAHs in the environment include both natural and anthropogenic sources. The natural sources of PAHs are diagenic and biogenic, whereas anthropogenic sources of PAHs
occur through accidental or intentional release of petrogenic and pyrogenic PAHs. Pyrogenic PAH sources are more common compared to other sources of PAHs. Common sources of pyrogenic PAHs include combustion of motor, bunker and power plant fuels (Boehm, 2006).

Diagenic PAHs are produced through diagenesis processes, which occur in low temperatures after oxygen depletion. These processes primarily produces relatively individual PAHs, among which diagenic PAHs and the 5-ringed PAH, perylene, is most common (Boehm, 2006). PAHs produced by diagenesis can be distinguished by their simple composition with only few PAH species rather than complex multi-species compositions exhibited by the petrogenic and pyrogenic PAHs (Boehm, 2006).

Petrogenic PAHs comprise between 0.2 % to more than 7 % of typical crude petroleum, nevertheless the petrogenic PAHs are still abundant in the environment primarily because they tend to be resistant to the weathering (Boehm, 2006). The formation of petrogenic PAHs differ from diagenic PAHs due to the higher temperature and longer period of formation. A main feature of petrogenic PAHs is the types of PAHs that exist in crude petroleum, which includes parent and alkylated PAHs (Boehm, 2006).

Pyrogenic PAHs are produced in high temperature environments by natural and anthropogenic processes (Boehm, 2006). Natural processes that produce pyrogenic PAHs include wood burning, forest fires, and anthropogenic processes involving combustion of fossil fuels such as gasoline, diesel, fuel oil, etc.

Biogenic PAHs are formed from PAH precursors by diagenesis or combustion of these compounds which are biosynthesized by microorganisms (Boehm, 2006). These compounds can be found in the environment and can interfere with the analyses because of their PAH characteristics.

2.5. Weathering Effects on Oil

Depending on the environmental conditions, oil will change physically and chemically in time as they are transported because of the environmental factors that lead to a process known as weathering. Wang and Christensen (2006) divide these processes into three groups as follows:
1. Physical processes: evaporation, emulsification, natural dispersion, dissolution, and other processes such as sedimentation, adhesion onto surface of suspended particulate materials, and oil-fine interaction
2. Chemical processes: photooxidation
3. Biological processes: microbial degradation

While the physical processes result in redistribution of oil components in different compartments of the environment, the photooxidation and microbial processes lead to chemical transformation and degradation of petroleum hydrocarbons, respectively (Wang & Christensen, 2006). Depending on the changes in concentration of compounds in the oil, Wang and Christensen (2006) divide weathered oil into following groups:

1. Lightly weathered oils (typically have decreases in the concentration of alkanes with small carbon numbers).
2. Moderately weathered (typically have major amounts of n-alkanes and low-molecular-weight isoprenoid compounds are lost).
3. Severely weathered oils (typically have significant loss of PAHs and the unresolved complex mixture (UCM) chromatogram is high).

In biological weathering, oil is biodegraded by indigenous microorganisms in the environment. This process is one of the most important oil clean up processes. Wang & Christensen (2006) determined the likelihood of biodegradation of compounds in the oil, and summarized the following list (presented in order of most to least likely of experiencing biodegradation):

- n-alkanes > BTEX and other monoaromatic compounds > branched and cyclo-alkanes > PAHs (lighter PAHs are more susceptible than larger PAHs and increase in alkylation level in the same PAH series decreases susceptibility to microbial attack) > biomarker terpanes and steranes

2.6.Gas Chromatography Techniques for Source Characterization

Investigators of oil spills use ratios of certain hydrocarbons to determine the source of the contamination. Crude and refined oil consist of mixtures of complex compounds and their ratios are specific to the origin of crude oil and processes used to refined oils. These ratios can be
attained using a gas chromatography flame ionization detector (GC FID) since GC FID is commonly used to determine the constituents in the oil.

2.6.1. Aliphatic Hydrocarbon Ratio

Aliphatic hydrocarbons are the most abundant hydrocarbon compounds in oil. The concentration of certain compounds and their ratios to other compounds are specific to various oils and can be used to distinguish between biogenic and petrogenic contamination sources. The differences between the biogenic and petrogenic sources are as follows:

1. Biogenic hydrocarbons have odd carbon-numbered alkanes abundant compared to even carbon-numbered alkanes in the range of n-C_{21}-n-C_{33}. This results in high carbon preference index (CPI) in biogenic hydrocarbons. The CPI is ratio of sum of odd carbon-numbered alkanes to even carbon-numbered alkanes (Wang et al, 2003).
2. Biogenic hydrocarbons have higher concentrations of pristanes compared to phytanes resulting in higher ratios of pristane/phytane than those of petrogenic hydrocarbons (Wang et al, 2003).
3. The $\sum n$-alkanes/n-C_{16} ratio can be used to determine the whether the contamination either petrogenic or biogenic. The ratio that is smaller than 30 indicates petrogenic alkane contamination and a ratio greater than 50 indicates biogenic alkane source (Gao and Chen, 2008).
4. The biogenic alkane hydrocarbons have low-molecular weight to high-molecular-weight ratios smaller than one where petrogenic alkanes have LMW/HMW ratios close to one. LMW/HMW ratios greater than 2 indicate fresh oil contamination (Gao and Chen, 2008).
5. The aliphatic isoprenoid ratios greater than 1 (such as pristane (Pr) and phytane (Ph)) are an indication of biogenic alkane sources. Values that are close or lower than one are an indication of a petrogenic source (Gao and Chen, 2008).

In addition, isoprenoid aliphatic hydrocarbon ratios can be used to determine the extent of weathering with biodegradation. An increase of Pr/n-C_{17} and Ph/n-C_{18} ratios is indication of
biodegradation of oil and the ratio can increase to higher than one when oil is extremely biodegraded (Snape et al., 2005; Gao and Chen, 2008).

2.6.2. Polycyclic Aromatic Hydrocarbons Ratio

Polycyclic aromatic hydrocarbons (PAHs) are more resistant to weathering than aliphatic hydrocarbons. Therefore, PAHs are one of the primary compounds used to distinguish between two sources of petroleum contamination. In addition, they are used to determine origin of contamination (such as biogenic, petrogenic or pyrogenic sources). The differences between petrogenic and biogenic PAHs sources are as follows:

1. Biogenic hydrocarbons chromatograms have biogenic cluster (olefinic hydrocarbons) in their gas chromatograms of aromatic fractions (Wang et al, 2003).
2. Biogenic hydrocarbons have PAH called perylene, which is specific to them (Wang et al, 2003).

The differences between petrogenic and pyrogenic PAHs sources are as follows:

1. Petrogenic PAHs have higher concentrations of alkyl PAHs (e.g. C1-Naphthalenes) compared to parent PAHs (e.g. Naphthalene). Pyrogenic PAHs have higher concentrations of parent PAHs (e.g. Chrysene). (Boehm, 2008; Wang et al, 2003)
2. Pyrogenic PAHs mostly consist of 4, 5 and 6+ ringed PAHs than petrogenic PAHs (Boehm, 2008; Wang et al, 2003).
3. The ratio of phenanthrene to anthracene (P/A) is used to distinguish between petrogenic and pyrogenic source contamination. If P/A> 10, the contamination source is petrogenic and if P/A<10, contamination source is pyrogenic (Boehm, 2008; Wang et al, 2003).

The differences between two petrogenic sources are as follows:

1. Depending on the refined oil type, the concentration found in petroleum oil differs (e.g., Bunker C has higher percentage of PAHs compared to Diesel) (Wang et al., 2008). In addition, refined oils have different concentrations of certain PAHs (e.g. Jet B fuel PAHs consist of 99% of naphthalene) (Wang et al, 2003).
2. The weathering of the oil alters and changes the chemical composition of the oil. Therefore, double ratio of alkylated dibenzothiophenes and phenanthrenes (C2D/C2P
versus C3D/C3P) can be used to determine the source of the spill, without any impacts of the weathering effects (Boehm et al., 1997; Wang et al, 2003).

2.6.3. Unresolved Complex Mixture

Unresolved complex mixtures (UCM) are found almost in all gas chromatograms of crude oil and its products. The UCM is a signature of oil contamination since it is only found in petroleum oil and can be used to distinguish the oil contamination (Wang et al, 2003). In addition, UCM chromatograms are unique to different type of oil depending on their origin and process they undergone (Wang et al, 2003). Therefore, UCM gas chromatograms can be used to distinguish between two oil contamination sources.

2.7. Absorbance and Fluorescence Spectrophotometry for Detection Oil Contamination

Distinguishing the source of crude or refined oil contamination with Gas Chromatography (GC) techniques is expensive and time consuming. Samples to be analyzed in GC needs to be extracted from water or soil, cleaned of interfering compounds and fractionated to its compounds. On the other hand, fluorometric analyses do not require sample preparation and fluorometric analyses can be performed on the field. The aromatic hydrocarbon fraction can be used to distinguish between several sources of the oil contamination by their fluorescence results. As was mentioned in Section 1.1. (on the chemical composition of oil), depending on origin and refining processes, oil will have a different concentration of compounds contributing to the fluorescence. Therefore, each oil product will demonstrate different degrees of fluorescence.

2.7.1. Absorbance Spectrometry

The absorption of light involves increase in energy of a molecule from the lowest energy state (ground state) to a higher energy state (excited state) by receiving energy from the light. Crude oil and its products consist of aromatic hydrocarbons, which absorb the light in a certain range of wavelengths. In order to understand the effectiveness of absorbance spectra on distinguishing the crude oils, Evdokimov and Losev (2007) analyzed two different types of oil (“Sour Heavy” type and “Sweet Light” type crude oil). Their analyses demonstrated the difference between the
absorbance spectral curves for these two crude oils. In addition, their analyses demonstrated that dilution of the crude oil affects their absorbance spectra and they suggested that it is due to difference in concentration of dissolved asphaltene in diluted samples.

2.7.2. Fluorescence Spectrometry

Fluorescence is the absorption of a photon by a molecule, which leads to an increase in energy, which leads to a molecule to rise from the ground state to an excited state, and the emission of photon, which leads to a return in energy to the ground state. The process in which the energy of molecule reaches an excited state is called excitation, and the process in which the energy of molecule returns back to the ground state is called emission. The aromatic hydrocarbons (e.g. naphthalene, anthracene, etc.) in crude oil are fluorescent molecules. Therefore, the fluorescence of the aromatic hydrocarbons in oil can be used to characterize oil contamination. There are several methods used to characterize and compare different oil types. Some of the techniques include are steady-state fluorescence spectroscopy, fluorescence lifetime measurement, synchronous scan fluorescence spectra and time-resolved fluorescence spectra.

2.7.2.1. Steady-state Fluorescence Spectroscopy

Steady-state fluorescence measurement is performed by constantly illuminating the sample with light and measuring excitation and emission spectra results (Lakowicz, 2006). This is the most widely used measurement because of its simplicity and inexpensiveness. Thruston and Knight (1971) used steady state fluorescence to distinguish different oil samples from each other. Oil samples were excited at 340 nm and emission spectra were measured from 360 nm to 440 nm. They compared the samples’ maximum intensity and intensity ratios. In addition, they were able to detect weathering effects on the fluorescence of the oil samples. They used two weathering effects to determine the extent of change of fluorescence of the oil. First, they analyzed evaporation of low-boilers compound, which demonstrated no significant change in fluorescence results. Second, they used decomposition by the sunlight to demonstrate significant changes in the intensity and shape of the emission spectrum. This demonstrates that decomposition weathering affects the fluorescence of the oil.
2.7.2.2. **Time-resolved Fluorescence Spectroscopy**

Time-resolved fluorescence measurement is a fluorescence analysis techniques that involves the illumination of samples with time-varying pulses of light, along with the measurement of the decay in intensity (Lakowicz, 2006). Hegazi and Hamdan (2002) used specific time gates at certain excitation spectra with a time-resolved fluorescence (TRF) spectra technique. In this method, Hegazi and Hamdan (2002) developed contour diagrams as functions of wavelength and time gates simultaneously. They were able to distinguish between different API grades of oil using general trends on contour diagrams and unique features for the same API grade oil. They were also able to distinguish between different API grades of oil using area ratio under the intensity curves but this were successful only in early time gates. Using area ratios, they found that, as the API grade value decreased, the area decreased. This approach was successfully used to distinguish between different values of API prepared in the lab, but the approach performed poorly with samples collected from the environment.

2.7.2.3. **Fluorescence Lifetime Measurement**

Lifetime measurement is one of the types of time-resolved fluorescence spectroscopy measurements where the time the molecule spent at excited state is measured (Lakowicz, 2006). Ryder et al. (2002) used fluorescence lifetime data of the oil samples to find a correlation between API grade, aromatic concentration and fluorescence lifetime. They found the existence of a close relationship between API grade and average lifetime, which has lower deviation then relation of aromatic concentration to average lifetime. In addition, the average lifetime ratios of certain emission spectra were correlated with concentrations of aromatic constituents in oil samples, and the ratios were correlated to the API grade of the oil. Therefore, lifetime fluorescence was found to be more useful for characterization of aromatics than the other methods described previously.

Interpretation of results from the fluorescence of oil samples can be challenging since the solvent that the contaminant is dissolved in can fluorescence and interfere with the results. Therefore, it is necessary to choose an optimal fluorescence range for which the solvent will not interfere with fluorescence of the oil. Liping et al. (2005) analyzed fluorescence of different types of water
without oil contamination. Analyses showed that water without any kind of contamination demonstrated peaks on the emission spectrum. Therefore, accounting for the effect of the fluorescence of the water on the data can be difficult task.

Another aspect of the solvent is the type of the solvent used to dissolve the oil. Holmes-Smith et al. (2012) analyzed oil with different grades using different approaches that incorporated fluorescence techniques to develop a method for distinguishing oil samples. In this analysis, they used polar, non-polar, aromatic and chlorinated solvents to dilute the oil sample. The fluorescence results showed different spectral curves for each sample. Holmes-Smith et al. (2012) inferred from the results that using different solvents could be used as a method for fingerprinting oil since each solvent dissolves certain component of the oil, which makes fluorescence curve specific for the oil.

2.7.2.4. The Effects of Oil Concentration to the Fluorescence

Depending on the type of oil, the oil can vary between yellow, brown and dark brown in color. However, in general concentrated oil is often opaque. Therefore, to decrease interference from opacity the oil samples have to be dissolved in solvent. The research of Steffens et al. (2011) demonstrated the importance of the opacity in fluorometric analyses for oil contamination. Steffens et al. (2011) measured emission spectrum of different concentration of the same oil at excitation frequencies of 350, 450 and 532 nm. The emission spectra results demonstrated a decrease in intensity with increasing oil concentration. In addition, emission spectra showed differences when oil concentration reached to a certain concentration even though it was same oil.

2.7.2.5. The Effects of Oil-water Emulsions on Fluorescence

Another feature of the oil to be considered for analysis with fluorescence techniques is the formation of emulsions, since oil spills in water will often float or form emulsions with the water and sink. Emulsions of the oil are much more difficult to manage since they are difficult to detect and identify. Therefore, Baszanowska et al. (2013) used fluorescence and absorbance spectra to detect oil in oil-in-water emulsions. They used a similarity ratio between spectra for five different types of oil with different concentrations to develop fluorescence and absorbance
spectra. The similarity ratio was successfully used for fluorescence since different concentrations of the same oil had a higher similarity ratio as compared to the ratios for different oil types. In the case of absorbance spectrum, no reasonable similarity was detected.

Liping et al. (2005) demonstrated that a mineral oil-water intermixture had optimal results for identifying oil samples using fluorescence excitation spectrums 254 and 360 nm and emission spectrums between 360 nm to 460 nm. The 10AU field fluorometer uses two different wavelength kits to measure oil contamination in the water. These kits include the short wavelength kit, which has excitation spectra at 254 nm and an emission spectral range between 300-400 nm, and a long wavelength kit, which has an excitation spectral range between 300-400 nm and emission spectral range between 410-600 nm. Accordingly, the Liping et al. (2005) results demonstrate that 10 AU field fluorometer can be used to detect oil contamination in the water.

2.8. Monitoring Sites

The sites for monitoring were chosen to provide a few cases with different types of oil contamination. The samples that collected from the sites include crude oil from the Deepwater Horizon Oil Spill, water and soil samples from the Bayou Corne sinkhole and water samples from the Fisherville Mill Site. Therefore, some background information is included here.

2.8.1. Deepwater Horizon Oil Spill

The Deepwater Horizon Oil Spill happened on April 20 2010 in Gulf of Mexico. Spilled crude oil was entering to the water through the exploration well. The crude oil was characterized as sweet oil with less concentration of sulfur and polycyclic aromatic hydrocarbons (PAHs) and high concentration of alkanes (NOAA, 2010). More information on the details and contamination associated with this spill can be found on the website of National Oceanic and Atmospheric Administration of United States (http://response.restoration.noaa.gov/deepwaterhorizon/).
2.8.2. *Bayou Corne*

Bayou Corne sinkhole in Louisiana was discovered on August 3 2012 where the land above the salt domes collapsed making a sinkhole. The residents living close to sinkhole smelled the presence of sweet crude oil in the air. Therefore, water and soil samples were collected from the site to be analyzed for presence of oil contamination. More information on the details and contamination associated with this spill can be found on the website of Louisiana Department of Environmental Quality Louisiana United States (http://www.deq.louisiana.gov/portal/bayoucorne.aspx).

2.8.3. *Fisherville Mill Site*

The Fisherville Mill site is located at 60 Main Street in Grafton, Massachusetts and listed as a Tier 1 Disposal Site. The site changed ownership several times and was used for industrial and textile fabrication and warehouse storage until 1986 when the operations ceased (Woodard & Curran, 2008). During its operation several products such as cotton goods, fabrics, aluminum goods, metal parts, and foam rubber were manufactured at the site (Woodard & Curran, 2008). The mill was using hydropower from the canal from 1832 until 1881 when it was destroyed with fire (Woodard & Curran, 2008). In 1891, the mill was rebuilt. In the 1940s underground storage tanks (USTs) were installed to be used as for heating fuel to power steam boilers (Woodard & Curran, 2008). In addition, site had dye ponds where wastewater from various processes was discharged until 1960. After the operations stopped in 1986, site investigations and cleanup activities continued until 1999, when fire destroyed the former mill building (Woodard & Curran, 2008). After the fire, thorough site investigations and cleanup activities are still being conducted.

The primary sources of polycyclic aromatic hydrocarbons (PAHs) are considered to be underground storage tanks (USTs) with estimated sizes of 20,000 gallons and dye ponds in the northern portion of the site (Woodard & Curran, 2008). In these USTs, No. 4 and No. 6 fuel oils were stored until their removal in 1999 (Woodard & Curran, 2008). In addition, on the site there was a 500-gallon gasoline UST on the site until its removal on 1987 (Woodard & Curran, 2008). On the site, other operations led to contamination with oil hazardous material (OHM). These
operations include steel cleaning with unknown chemicals and aluminum lawn production processes which utilized petroleum based compounds (Woodard & Curran, 2008).

During the excavation of one of the 20,000 gallon USTs, the tank was found to have holes in it (Woodard & Curran, 2008). Leakage from this UST had affected the soil underneath it. The region into which the oil leaked was revealed to be at least 15 feet laterally from the USTs and at least 15 feet vertically from bottom of the excavation (Woodard & Curran, 2008). After the detection of the contaminated soil, 5,000 cubic yards of petroleum-impacted soil were excavated from the spill location (Woodard & Curran, 2008). Samples collected from the USTs spill location demonstrated the presence of a non-aqueous phase liquid (NAPL) with predominantly No. 6 fuel oil (Woodard & Curran, 2008). Oil was detected in the Blackstone River on January 28, 1977 (Woodard & Curran, 2008). Since all operations ceased after 1986, no operations have introduced new contamination source until a fire occurred in 1999. The fire destroyed the mill building and introduced new contaminants to the site. After the fire, the amount of material removed included 3,312 tons of asbestos containing material (ACM) and 3,226 tons of lead contaminated ash and debris (Woodard & Curran, 2008).

Currently, some of the water from the Blackstone Canal on the site is being treated by a treatment system called the "Eco-Machine", which was developed by John Todd Ecological Design to remove organic contaminants from the water. The treatment processes included algal, plant, and fungal growth processes maintained in cells inside of a green house. More information on the details and contamination associated with this spill can be found on the web site of John Todd Ecological Design (http://toddecological.com/). Given the nature of the contamination and efforts to mitigate the contamination at the Fisherville Site, the site provides a relevant context for this investigation.
3. METHODOLOGY

The objectives of this research are to understand the characteristics of organic transport in a linked surface-water/ground-water system and develop some practical approaches using fluorometry to characterize the pathways of organic transport. This chapter describes the approach and methods used to meet these objectives. The approach included site selection and sampling, and preparation, modeling, analysis of samples, and comparison of results. The understanding of the characteristics of the transport of organics requires with detection and definition of the organic chemicals. Characterization of organics can be achieved by a variety of different analytical methods, depending on the organic material chemical characteristics. For this research, the following equipment and methods were used: a 10 Au Field Fluorometer for raw fluorometric absorbance, Shimadzu UV 2100U for absorbance spectra, Perkin Elmer LS 50B for fluorescence spectra and Agilent Technologies 6890 Series Gas Chromatography System with a flame ionization detector (FID) for detailed characterization of the samples. Site selection, sampling and preparation are described in Sections 3.1 through 3.3, the modeling described in Section 3.4, and the analysis of samples are described in Sections 3.5 through 3.8.

3.1. Site Selection

Achieving the objectives of the research required the selection of samples with different constituents for comparison, preparing collected samples for analyses and analyzing prepared samples using different techniques. The samples were selected to provide a variety of contaminant characteristics. Samples include samples collected from the Fisherville Mill Site in Grafton, MA, which has contamination due to weathered fuel oil No. 6, a sample of Gulf of Mexico crude oil associated with the Deepwater Horizon Spill, and water and soil samples containing oil and other contaminants collected from the Bayou Corne site in Louisiana. The Deepwater Horizon crude oil and Bayou Corne samples provided different compositions of PAHs that were helpful for comparisons. Since specific site/source characteristics were not available for these sites, the site details are not discussed further. Since the Fisherville Mill site was accessible and relatively well characterized, it was sampled and analyzed in more detail for this research. Figure 3.1 shows the detailed map of the Fisherville Mill Site.
generally flows in the southeasterly direction from the spill site (designated as the former dry well source area in Figure 3.1) and Blackstone Canal towards the Blackstone River.

Figure 3.1 Fisherville Mill Site Map (by Woodard & Curran 2008)
3.2. Groundwater Flow Modelling

Groundwater flow was modelled using Visual Modflow Flex 2014. Data for the modelling was obtained from the report of Woodard & Curran (2008) and the model developed by Coler & Colantonio (2003). The start date for their model was set to 19th of September 2002. Specific storage ($S_s$) was set to 0.0001 ft$^{-1}$ and the specific yield ($S_y$) was set to 0.25. The grid size was set to 215 columns and 100 rows. The surface of the model was developed using elevation contour maps of Fisherville Mill Site. Surface layers are shown in figure 3.2. From the contour maps, it was revealed that there were four geological layers on the Fisherville Mill Site. The first, upper layer of the site is a layer of sand covering the middle and northeast area of the site. The second layer is a peat layer below the first layer center of the site. Sand and gravel covers all of the area of the third layer and cover major parts of the first and second layer as well. The last, lowest layer of the site is bedrock.

![Figure 3.2 Fisherville Mill Site surface layers](image)

Figure 3.2 Fisherville Mill Site surface layers
3.2.1. Conductivity and Initial Head (Coler & Colantonio, 2003)

Conductivity for the layers was set to different values depending on the geological material. The first layer is consists of two separate geological materials with two different conductivities. These geological materials are sand with a hydraulic conductivity of 500 ft/day and a sand & gravel mixture with a hydraulic conductivity of 1500 ft/day. The second layer is consists of sand & gravel mixture and peat layer. The peat layer is a layer that has a low permeability; therefore, the conductivity was set up to be similar to that of bedrock (1 ft/day). The initial head of the model was set to 278 feet, which is the same as the highest stage of the Blackstone River.

3.2.2. Boundary Conditions (Woodard & Curran, 2008; Coler & Colantonio, 2003)

The boundary condition of the north side of the model was set with a head of 284 feet and the south side of the model was set with a head of 278 feet. The northwest boundary of the model was set decrease from 284 feet to 278 feet and northeast boundary of the model was set decrease from 284 feet to 276 feet. The stage for the Blackstone River was set such it was 278 feet in the north and decrease to 276 feet at south. The river bottom elevation was set such that it was 276 feet in the north and decreased to 274 feet at the south end. The conductance of the river was given as 15000 ft²/day; therefore, the hydraulic conductivity of the river bottom was calculated using equation 63-a as listed in the MODFLOW Reference Manual (1996). Accordingly, the conductivity of the river bottom was calculated to be 150 ft/day.

The Blackstone Canal stage was set to 277 feet and river bottom was set to 275.5 feet with calculated conductivity of 2.5 ft/day using equation 63-a from MODFLOW Reference Manual (1996). Recharge for the model was set to 15 in/year (EPA, 2006).

3.2.3. Wells

Two pumping wells for the South Grafton Water Supply District (SGWD) are located close to the site and as such can affect the groundwater flow at the site. These wells are SGWD # 2 and SGWD # 3 with pumping rates of 150 GPM and 450 GPM, respectively. These wells provide water to the Town of Grafton. As such, there is a major concern in regards to the potential for
contaminant transport that may result in contamination of drinking water. Table 3.1 shows the elevations, pumping schedule and pumping rate as was entered to the model.

Table 3.1 Pumping well data (Woodard & Curran, 2008)

<table>
<thead>
<tr>
<th>Well Id</th>
<th>Elevation (ft)</th>
<th>Well bottom (ft)</th>
<th>Screen Id</th>
<th>Screen top Z (ft)</th>
<th>Screen bottom Z (ft)</th>
<th>Pumping start date</th>
<th>Pumping end date</th>
<th>Pumping rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGWD 3</td>
<td>280.00</td>
<td>41.00</td>
<td>3.00</td>
<td>259.00</td>
<td>249.00</td>
<td>9/19/2002</td>
<td>5/1/2003</td>
<td>-450.00</td>
</tr>
<tr>
<td>SGWD 2</td>
<td>280.00</td>
<td>41.00</td>
<td>2.00</td>
<td>259.00</td>
<td>249.00</td>
<td>9/19/2002</td>
<td>5/1/2003</td>
<td>-150.00</td>
</tr>
</tbody>
</table>

Six observation wells were included in the model, to allow for backtracking to the origin of the contamination in these wells. These wells were used to collect samples and analyze for the oil contamination. The observation wells were chosen to understand contaminant transport from Blackstone Canal to Blackstone River. Therefore, these wells are located between these water bodies. Table 3.2 shows the elevations and observed heads that was entered to the model.

Table 3.2 Observation well data (Woodard & Curran, 2008)

<table>
<thead>
<tr>
<th>Well Id</th>
<th>X</th>
<th>Y</th>
<th>Elevation (ft)</th>
<th>Well bottom (ft)</th>
<th>Logger Id</th>
<th>Logger Z (ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW-1D</td>
<td>1000</td>
<td>200</td>
<td>284</td>
<td>49.5</td>
<td>1</td>
<td>283</td>
</tr>
<tr>
<td>MW-31D</td>
<td>1325</td>
<td>350</td>
<td>280</td>
<td>59</td>
<td>1</td>
<td>279.55</td>
</tr>
<tr>
<td>MW-31S</td>
<td>1320</td>
<td>345</td>
<td>281.72</td>
<td>13.5</td>
<td>1</td>
<td>281.6</td>
</tr>
<tr>
<td>MW-30D</td>
<td>1175</td>
<td>450</td>
<td>284.9</td>
<td>43.3</td>
<td>1</td>
<td>284.55</td>
</tr>
<tr>
<td>MW-45S</td>
<td>1075</td>
<td>650</td>
<td>280</td>
<td>9</td>
<td>1</td>
<td>279.3</td>
</tr>
<tr>
<td>MW-29M</td>
<td>1010</td>
<td>300</td>
<td>282</td>
<td>45</td>
<td>1</td>
<td>281.8</td>
</tr>
</tbody>
</table>

3.3. Sample Collection and Storage

Surface water and groundwater samples were collected from the Fisherville Mill Site and stored in 1-liter amber glass bottles with Teflon-lined screw caps, 500 mL amber glass bottles with Teflon-lined screw caps, 120 mL amber plastic bottles, 60 mL amber plastic bottles and 40 mL
amber glass bottles with Teflon-lined screw caps. Surface water samples were collected from the spill location and from three different locations along the Fisherville Canal using a Van Dorn horizontal water sampler (shown in Figure 3.3). During sample collection, water bottles were rinsed three times with sample water from the location. This procedure helps to avoid cross contamination. Surface water locations were selected at three locations along the Fisherville Canal downstream of the spill location, with location 1 being closest to spilled location and 3 being furthest (shown in Figure 3.4).

![Figure 3.3 Van Dorn horizontal sampler (Photo: Google Image, 2014)](image)

Groundwater samples were collected from six different wells. Wells were chosen depending on their depth and location on the groundwater flow path. The water samples were collected from wells using a heavy-duty submersible sampling pump (shown in Figure 3.5). Between collections of each water sample, the pump was operated using deionized water, providing more than three rinses to avoid any cross contamination from well to well.
After collection, the water samples were stored in a storage box (cooler) with ice to cool down samples to $4 \pm 2$ °C during their transportation from the site to the laboratory. Samples were stored in the refrigerator in the laboratory. The holding time specified for water samples for organic analyses is summarized in Table 3.3.
### Table 3.3 Holding Times (MA DEP EPH Method Manual, 2004)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Type of Analyses</th>
<th>Container</th>
<th>Holding Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous Sample</td>
<td>Extractable Petroleum Hydrocarbon Analyses</td>
<td>1-Liter amber glass bottle with Teflon-lined screw cap</td>
<td>Samples must be extracted within 14 days and extracts analyzed within 40 days</td>
</tr>
<tr>
<td>Aqueous Sample</td>
<td>Extractable Petroleum Hydrocarbon Analyses</td>
<td>500 ml amber glass bottle with Teflon-lined screw cap</td>
<td>Samples must be extracted within 14 days and extracts analyzed within 40 days</td>
</tr>
<tr>
<td>Aqueous Sample</td>
<td>pH</td>
<td>120 ml amber plastic</td>
<td>Samples must be analyzed within a day</td>
</tr>
<tr>
<td>Aqueous Sample</td>
<td>Conductivity</td>
<td>60 ml amber plastic</td>
<td>Samples must be analyzed within a day</td>
</tr>
<tr>
<td>Aqueous Sample</td>
<td>Dissolved Oxygen</td>
<td>300 ml DO bottle</td>
<td>Samples must be analyzed within a day</td>
</tr>
<tr>
<td>Aqueous Sample</td>
<td>Absorbance and Fluorescence analyzes of PAHs</td>
<td>40 ml amber glass bottle with Teflon-lined screw cap</td>
<td>Samples must be extracted within 14 days and extracts analyzed within 40 days</td>
</tr>
</tbody>
</table>

### 3.4. Sample Preparation

Prior to completing the gas chromatography and, as appropriate, the other analyses, samples were extracted and fractionated to aromatic and aliphatic fractions. Extraction was used to separate the contaminant from its dissolved matrix and concentrate of the sample to increase its concentration so it is above the detection limit of equipment. In addition, extraction was used prior to fractionation of the oil contaminant to its aliphatic and aromatic fractions for gas
chromatography analysis. The extraction and fractionation methods are explained in Sections 3.7.1, 3.7.2 and 3.7.3.

3.5. Analyses Using the 10 AU Field Fluorometer

A 10 AU Turner Designs field fluorometer was used to measure raw fluorometric absorbance of the contaminants in water. A field fluorometer uses two ranges of spectra: short wavelength range and long wavelength range to measure relative concentration of fluorescing organics contaminant in water. This equipment was designed to allow measurements to be obtained both in the field and in the lab. It has the capability to measure discrete samples and continuous flow, which provides opportunity to collect data across the river or a lake in real time.

3.5.1. Operating Procedure for Field Fluorometer

The field fluorometer measures samples in a limited range of spectra depending on the filter installed. Therefore, prior to measuring the samples, the equipment requires installation of required filters for analyses. In addition, a lamp needs to be installed to provide the required spectrum. The lamp provides the light that passes through an excitation filter that filters light such that it matches the wavelength range that is specific to the filter. Light passed through excitation filter excites fluorescence of the materials in the sample. The excited materials emit light that passes through the emission filter, which filters the emitted light to the wavelength that is specific to the filter. The filtered light travels to photomultiplier tube that sends a signal to digital display. Figure 3.6 shows the measuring operation of fluorometer.
Table 3.4 lists types of lamps and filters with their spectrum range depending on contaminant type. As shown on the table 3.4, oil measurements can be completed with two different ranges of spectrum: the analyses called the short wavelength and long wavelength analyses. Crude oil and refined oil emits light in the range of 350 nm-650 nm as shown on Figure 3.7. Therefore, for this research, both short and long wavelength analyses were used in the oil measurements.
Table 3.4 Lamp and filter type for 10 AU field fluorometer (Turner Designs, 1999)

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Ammonium or Colored/Fluorescent Dissolved Organic Matter (CDOM/FDOM)</td>
<td>1100-101</td>
<td>Standard</td>
<td>300-450nm</td>
<td>10-303</td>
<td>034-004</td>
<td>*50FS10-25</td>
<td>500nm</td>
<td>500nm</td>
<td>500nm</td>
<td>50-049</td>
<td>T12/24R</td>
<td>10-AU-904</td>
</tr>
<tr>
<td>Extractive and in-vivo Chlorophyll (Acidification method)</td>
<td>1100-100</td>
<td>Red</td>
<td>165-470nm</td>
<td>10-637R</td>
<td>034-004</td>
<td>*65FS10-25</td>
<td>650nm</td>
<td>650nm</td>
<td>650nm</td>
<td>50-045</td>
<td>T12/24R</td>
<td>Not Required</td>
</tr>
<tr>
<td>Extractive Chlorophyll (Non-acidification method)</td>
<td>1100-100</td>
<td>Red</td>
<td>165-470nm</td>
<td>10-404R</td>
<td>034-0395</td>
<td>*60FS10-25</td>
<td>600nm</td>
<td>600nm</td>
<td>600nm</td>
<td>50-039</td>
<td>T12/24R</td>
<td>Not Required</td>
</tr>
<tr>
<td>In-Vivo Chlorophyll (Water with high dissolved organic matter (DOM) and chlorophyll a)</td>
<td>1100-100</td>
<td>Red</td>
<td>165-470nm</td>
<td>10-496R</td>
<td>034-0395</td>
<td>*60FS10-25</td>
<td>600nm</td>
<td>600nm</td>
<td>600nm</td>
<td>50-039</td>
<td>T12/24R</td>
<td>Not Required</td>
</tr>
<tr>
<td>Fluorescein</td>
<td>1100-101</td>
<td>Standard</td>
<td>300-450nm</td>
<td>10-698R</td>
<td>034-0600</td>
<td>*60FS10-25</td>
<td>600nm</td>
<td>600nm</td>
<td>600nm</td>
<td>50-045</td>
<td>T12/24R</td>
<td>Not Required</td>
</tr>
<tr>
<td>Phycocyanin</td>
<td>1100-101</td>
<td>Standard</td>
<td>300-450nm</td>
<td>10-304</td>
<td>034-0544</td>
<td>*54FS10-25</td>
<td>540nm</td>
<td>540nm</td>
<td>540nm</td>
<td>50-045</td>
<td>T12/24R</td>
<td>Not Required</td>
</tr>
<tr>
<td>Phycocyanin</td>
<td>1100-100</td>
<td>Red</td>
<td>165-470nm</td>
<td>10-305</td>
<td>034-0544</td>
<td>*54FS10-25</td>
<td>540nm</td>
<td>540nm</td>
<td>540nm</td>
<td>50-045</td>
<td>T12/24R</td>
<td>Not Required</td>
</tr>
<tr>
<td>Rhodamine WT</td>
<td>1100-101</td>
<td>Standard</td>
<td>300-450nm</td>
<td>10-641R</td>
<td>034-0500</td>
<td>*50FS10-25</td>
<td>500nm</td>
<td>500nm</td>
<td>500nm</td>
<td>50-046</td>
<td>T12/24R</td>
<td>Not Required</td>
</tr>
<tr>
<td>Oil, Short Wavelength QUARTZ CUVETTE or TEST TUBE REQUIRED</td>
<td>1100-101</td>
<td>Standard</td>
<td>300-450nm</td>
<td>10-301R</td>
<td>034-0960</td>
<td>124FS10-25</td>
<td>1240nm</td>
<td>1240nm</td>
<td>1240nm</td>
<td>50-045</td>
<td>T12/24R</td>
<td>10-AU-904</td>
</tr>
<tr>
<td>Optical Brighteners</td>
<td>1100-101</td>
<td>Standard</td>
<td>300-450nm</td>
<td>10-306</td>
<td>034-2392</td>
<td>*60FS10-25</td>
<td>600nm</td>
<td>600nm</td>
<td>600nm</td>
<td>50-045</td>
<td>T12/24R</td>
<td>10-AU-904</td>
</tr>
<tr>
<td>Turbidity</td>
<td>1100-101</td>
<td>Standard</td>
<td>300-450nm</td>
<td>10-307R</td>
<td>034-0000</td>
<td>*60FS10-25</td>
<td>600nm</td>
<td>600nm</td>
<td>600nm</td>
<td>50-046</td>
<td>T12/24R</td>
<td>10-AU-904</td>
</tr>
</tbody>
</table>

*Indicates Filter Mfr. Part # Reference .

Figure 3.7 Emission spectra range for crude oil and their products (Steffens et al., 2011)
3.5.2. **Short Wavelength**

Oil analyses for short wavelength range were completed using a 10-046 clear quartz lamp and filters, including the 10-300 soft glass reference filter, the 034-0860/254FS25-25 excitation filter and the 10-069R emission filter. The reference filter allows light with wavelengths greater 300 nm, the excitation filter allows light with wavelength of 254 nm to pass and the emission filter allows light with wavelengths in the range 300-400 nm (Turner Designs, 1999). After the required filters were installed the fluorometer was calibrated using the NDSA (1,5-naphtalene disulfonic acid disodium salt) standard, as suggested by Turner Designs.

3.5.3. **Long Wavelength**

Oil analyses in the long wavelength range were completed using a 10-049 near-UV lamp and filters, which included a 10-300 Soft Glass reference filter, a 10-069R excitation filter and a 10-110R-C emission filter. The reference filter allows light with wavelengths greater 300 nm to pass, the excitation filter allows the light with wavelength in the range of 300-400 nm to pass, and emission filter allows light with wavelength in the range of 410 to 600 nm to pass (Turner Designs, 1999). After the required filters were installed, the fluorometer was calibrated using PTSA (1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt) standard suggested by Turner Designs.

3.5.4. **Field Fluorometer Standards for Oil Measurements**

As was mentioned above, after installing the filters, the fluorometer requires calibration using standards or samples best representing the contaminant. For oil measurements, the NDSA and the PTSA standards were used to calibrate the fluorometer.

3.5.5. **NDSA (1,5-naphtalene disulfonic acid disodium salt)**

NDSA was used as a standard to calibrate the fluorometer for detecting refined oils and fuels in water with short wavelengths. Tuner Designs describes NDSA as a nontoxic, nonflammable, nonreactive and non-hazardous material emitting wavelengths between 300 and 400 nm when excited with deep UV (<300 nm) light. The concentration of the NDSA used during the calibration of the fluorometer was 400 ppb. The steps for fluorometer calibration can be found in
Appendix A1. When the fluorometer was initially calibrated with a high concentration of NDSA standard, Fisherville Mill Site samples demonstrated negative results. Therefore, the concentration of the NDSA standard was decreased to a lower concentration, which allowed for successful calibration. The calibration curve was developed using different concentrations of NDSA and was used to determine the equivalent concentration of fluorescence compounds in water sample as shown on figure 3.8.

![NDSA Calibration Curve](image)

**Figure 3.8** NDSA Calibration Curve

An equation to calculate the equivalent concentration of the fluorescence of organic matter in the water sample was developed using the calibration curve shown on figure 3.8. The equations are as follows:

\[ C_{\text{fluorescence}} = 0.3182 \times C_{\text{NDSA}} \]  
(Equation 1)

\[ C_{\text{NDSA}} = \frac{C_{\text{fluorescence}}}{0.3182} \]  
(Equation 2)

Where \( C_{\text{fluorescence}} \) is the readout concentration of the fluorescence compound in parts per billion (PPB) and \( C_{\text{NDSA}} \) is the equivalent concentration of the fluorescence compound in part per billion (PPB).
Using equation 2 and the fluorescence readout of samples, an equivalent concentration of the contaminant was calculated and used in comparison to results from other methods. The calculated equivalent concentrations are shown in table 4.2.

3.5.6. PTSA (1,3,6,8-pyrenetetrasulfonic acid tetraborate tetrasodium salt)

PTSA was used as a standard to calibrate the fluorometer for detecting crude oil in water using fluorescence over long wavelengths. Turner Designs (2011) describes PTSA as a nontoxic, nonflammable, nonreactive and non-hazardous material emitting wavelengths between 400 and 500 nm when excited with UV light. Calibration of the fluorometer with PTSA was performed using a concentration of 80 PPB of PTSA. The steps for fluorometer calibration can be found in Appendix A1. Using different concentrations of PTSA, a calibration curve was developed and used to determine an equivalent concentration of fluorescence compounds in water sample. This curve is shown in figure 3.9.

![PTSA Calibration Curve](image)

**Figure 3.9 PTSA Calibration Curve**

The equation to calculate an equivalent concentration of the fluorescence of organic matter in the water samples was developed using the calibration curve shown in figure 3.9. The equations are as follows:

\[
C_{\text{fluorescence}} = 0.0094 \times C_{\text{PTSA}} 
\]  
(Equation 3)
\[ C_{\text{PTSA}} = C_{\text{fluorescence}} / 0.0094 \] (Equation 4)

In these equations, \( C_{\text{fluorescence}} \) is the readout concentration of the fluorescence compound in parts per billion (PPB). \( C_{\text{PTSA}} \) is the equivalent concentration of the fluorescence compound in parts per billion (PPB). Using equation 4 and the fluorescence readout of samples, equivalent concentrations of contaminant were calculated and used in comparison to results of other methods. The calculated equivalent concentrations are shown in table 4.3.

### 3.5.7. Sensitivity of field fluorometer for oil measurements

The fluorometer requires adjustment of its sensitivity prior calibrating the instrument. Adjustment of sensitivity is completed by using known concentration of standard or sample best representing contaminant concentration. If the sensitivity is adjusted correctly, the exact concentration of the standard can be read after calibration. If the sensitivity adjusted with knob is not sufficient to accommodate the range of concentrations, then the sensitivity can be adjusted by changing the cuvette size. Turner Designs (1999) discuss in detail the cuvette sizes for sensitivity adjustment in the 10 AU Field Fluorometer Manual.

### 3.5.8. Calibration of field fluorometer

The fluorometer was calibrated using standards NDSA and PTSA. Concentration of the standard for calibration is important and depends on the expected concentration of the contaminant in sample water. If expected concentration of contaminant in the water sample is high, then fluorometer should be calibrated with a high concentration standard solution. If the expected concentration of contaminant is low, then fluorometer should be calibrated with low concentration of the standard solution. The required concentration of standard is shown in figure 3.10.
Absorbance spectra were collected to determine absorbance ranges of different oil types in the environment. The analyses were achieved by preparing samples with different concentrations and measuring their absorbance in the range between 200 nm and 800 nm. Absorbance spectra can be measured without requiring calibration of the equipment, which provides the opportunity to analyze the effectiveness of techniques and standards used in calibrating the field fluorometer. Figure 3.11 shows the absorbance spectrum of mixture of aromatic and aliphatic hydrocarbons standards. In addition, the spectrometer has the advantage of the use of blanks, which eliminates interference from the solvent. As was mentioned by Liping et al. (2005) in their research solvents also emit wavelengths that can interfere with contaminant emission spectrum.

The instrument’s absorbance highest value and absorbance spectrum range was configured to address expected absorbance results of the sample. After configuration, the base line was set using the solvent contaminant dissolved in. This procedure helps to eliminate interference from
the solvent. After the baseline was set, the samples were analyzed between spectrum ranges of 200 nm to 800 nm. Since samples, demonstrated absorbance in certain ranges the results was configured to the specific range to get more clear results, as shown in figure 3.11.

![Absorbance Spectra of Aromatic and Aliphatic Hydrocarbon Standard Mixture in DCM](image)

**Figure 3.11** Absorbance Spectra of Aromatic and Aliphatic Hydrocarbon Standard Mixture in DCM

### 3.7. Fluorescence Spectrometry

Fluorescence spectra were obtained using a Perkin Elmer LS 50B luminescence spectrophotometer. The Perkin Elmer LS 50B luminescence spectrophotometer measures excitation and emission spectra between 200 and 800 nm. Fluorescence spectra were analyzed for the samples to determine if the working range of fluorometer was effective for detection of oil contamination in the water. Fluorescence of the material can be measured without calibration of the equipment, although interference from the solvent cannot be eliminated in this equipment. Therefore, to determine interference from solvent matrix blanks with the solvent were analyzed prior running the sample. The fluorescence of the blank of dichloromethane solvent is shown at figure 3.12.

The fluorescence spectrometry analyses involved analyses of the samples over the spectral range of the excitation and emission spectra designated for the short wavelength and long wavelength kits used for the 10 AU field fluorometer. First, samples were analyzed by setting the excitation
spectra to 254 nm (the short wavelength kit’s excitation spectrum) and setting the emission spectra between 300-400 nm (the short wavelengths kit’s emission spectral range) and between 410-600 (the long wavelength kit’s emission spectral range). Second the samples were analyzed by setting the excitation spectral range between 300-400 nm (the long wavelength kit’s excitation spectral range) and emission spectra between 300-400 nm (the short wavelengths kit’s emission spectral range) and also between 410-600 (the long wavelength kit’s emission spectral range). For the final step, the fluorescence was scanned over a wide range with the excitation spectral range set from 200 to 800 nm and emission spectral range set from 200 to 800 nm. This allowed determination of the intensity for a full range of wavelengths, providing the opportunity to determine the effectiveness of the spectral ranges that were designated for the field fluorometer.

![Fluorescence Spectra of dichloromethane](image)

**Figure 3.12** Fluorescence Spectra of dichloromethane

### 3.8. Gas Chromatography with Flame Ionization Detector

Gas chromatography (GC) analyses were performed to determine the constituents of the water samples and origin of the contamination. These analyses were performed using an Agilent Technologies 6890 Series GC System using a RTX-5 SIL MS (30 meter, 0.32 mm inner diameter, 0.5-micrometer film thickness) column manufactured by Restek Corporation
(Bellefont, Pennsylvania). Prepared extracts were injected to the GC with an Agilent Technologies 7683 Injector and 7683 Autosampler. The flame ionization detector (FID) was used because of its ability to detect 16 PAHs from EPA priority list.

3.8.1. **Liquid/Liquid Extraction Procedure** *(MA DEP EPH Method, 2004; Z. Wang et al., 2002)*

Extracts were completed by adding 500 mL of water sample to a separatory funnel and 10 µl of the surrogate-spiking standard o-terphenyl diluted in 1.0 ml acetone. Water was allowed to sit 15 minutes prior adding 30 ml of methylene chloride and was shaken vigorously for at least 3 minutes with periodic venting since methylene chloride builds up pressure. After the vigorous shaking, the organic layer was separated by allowing water to sit for a minimum of 5 minutes. Extracts were repeated two more times using 30 ml of methylene chloride. The three solvent extracts were combined prior to passing the extract through a funnel containing anhydrous sodium sulfate to remove remaining water and natural organic matter. The anhydrous sodium sulfate was heated for at least 4 hours in an oven at 430 °C *(NWTPH-HCID, 1997)*. Afterwards the extract was concentrated to a volume of 1 ml under a gentle stream of nitrogen in air blowdown apparatus. When the extract reached volume of 1 ml, 10 ml of hexane was added to change the solvent for the fractionation step and was concentrated again to a volume of 1 ml under a gentle stream of nitrogen. After the extract was concentrated to desired volume, 10 µl of fraction surrogate standard 2-Fluorobiphenyl was added to the extract. Fractionation surrogate standard helps to measure effectiveness of fractionation method by measuring the quantity of standard passes through the silica gel.

3.8.2. **Soil Extraction Procedure** *(NWTPH-HCID, 1997)*

For the soil extraction procedure, 10 grams of contaminated soil was placed into a 40 ml VOA vial with 5 grams of anhydrous sodium sulfate, 10 µl of o-terphenyl and 10 ml of dichloromethane. The vial was capped and placed into sonic bath for 5 minutes. Then, the vial was taken out of the sonic bath and was shaken for approximately 1 minute. When the content of the vial was mixed, it was placed again to the sonic bath for another 5 minutes. The solvent above the soil was taken with a syringe and injected to the nitrogen air-blowdown instrument to
concentrate the sample to 1 ml. After the sample was concentrated to 1 ml, the sample was fractionated using the fractionation method.


Silica gel cartridges were pre-rinsed with 30 ml of hexane prior to usage. In case the silica gel cartridge had been used once before, silica gel cartridges were pre-rinsed with 30 ml of methylene chloride and 60 ml of hexane to eliminate cross contamination from previous runs. When the hexane for cleanup reached just above the column frit, 1 ml of the combined sample extract with fractionation surrogate standard was loaded to the column, and eluent was collected into a 25-ml volumetric flask labeled “aliphatic”. Just before the loaded extract reached the top of the column frit, the 19 ml of hexane was loaded to the column, so that a total of approximately 20 ml of hexane passed through the column. After the final load of hexane reached just above the column frit 20 ml of methylene chloride was loaded and eluent was collected into a 25-ml volumetric flask labeled “aromatics”. Afterwards the eluents were concentrated to a volume of 1 ml under a gentle stream of nitrogen. Prior to analyses by gas chromatography, 10 µl of internal standard 5-α-androstane was added to each extract. Samples were then ready for analysis by gas chromatography.


The temperature program of the gas chromatography was setup according to MA DEP EPH method. The Injector volume of the GC was setup to 1 µl and the syringe was washed prior to and after completing each sample run with the extract’s solvent to decrease the potential for cross contamination. The inlet of GC was heated up to 285 ºC and inner pressure was set to 15 psi with a total flow of nitrogen gas (N₂) of 4.5 mL/min. The oven’s initial temperature was set to 60 ºC and the hold time was at 1 minute. Then, the temperature was increased 6 ºC/min until it reached to 290 ºC and the hold time was 15 minutes. The temperature in the FID was set to 315 ºC with hydrogen (H₂) flow to 40 mL/min, airflow to 450 ml/min and make up flow of nitrogen (N₂) to 25 ml/min. The data were collected starting from 2.45 minute of total run time.
Figure 3.13 GC-FID chromatogram of 14 aliphatic hydrocarbons

Figure 3.14 GC-FID chromatogram of 17 aromatic hydrocarbons

Figure 3.13 and 3.14 shows the aliphatic hydrocarbon and aromatic hydrocarbons standards GC results using the above-described GC program. The results of the standards were successful demonstrating that the GC program can be used to detect aliphatic and aromatic hydrocarbons in prepared extracts.

As explained in Section 2.5, ratios of aliphatic and aromatic hydrocarbons are used to interpret and understand characteristics of the contamination due to organics. The ratio of $\sum n$-alkanes/n-16 was used to determine whether the source of contamination was either biogenic (biosynthesized by microorganisms or plants) or petrogenic (crude oil or its products) (Gao and Chen, 2008). If the ratio of $\sum n$-alkanes/n-16 was smaller than 30, the result indicates that the origin of the pollution is crude oil. If this ratio is greater than 50, the result indicates that the origin of aliphatic is biogenic (biosynthesized by microorganisms or plants) (Gao and Chen, 2008). Biogenic inputs do not normally indicate potential hazards to the environment since the input can be associated with degradation of plants and organisms. In addition, the ratio of low
molecular weight hydrocarbons to high molecular compounds (LMW/HMW) was used to determine the nature of the contamination. The LMW/HMW ratios close to one indicate contamination that is likely associated with an oil spill, and a LMW/HMW ratio that is greater than two likely indicate the presence of fresh oil contamination (Gao and Chen, 2008). Equations for the $\Sigma n$-alkanes/n-16 and LMW/HMW ratios as follows:

$$\Sigma n\text{-alkanes/n-16} = (C_9 + \ldots + C_{36}) / C_{16} \quad (\text{Equation 5})$$

$$\text{LMW/HMW} = (C_9 - C_{18}) / (C_{19} - C_{36}) \quad (\text{Equation 6})$$
4. RESULTS

This research used a set of comparisons between different analysis approaches to provide an assessment of fluorometric techniques to characterize contamination due to organics from petroleum hydrocarbons associated with oil discharges in the environment. This chapter presents the results of the analyses completed for three sets of samples, including crude oil associated with the Deepwater Horizon discharge, a sample from the Bayou Corne sinkhole, and the Fisherville Mill Site in Grafton, MA. In addition, aromatic hydrocarbon standard consisting of 17 PAHs were analyzed to compare to sample results. The results of each method demonstrated source of oil contamination. Since the Fisherville Mill site was accessible and well documented, the spatial distribution of contamination at this site is included. The results presented in this chapter include site characterization and model results for the Fisherville Site, and results using field fluorometry, absorbance spectrometry, fluorescence spectrometry, and gas chromatography.

4.1. Fisherville Site Monitoring

Samples were collected from the canal, groundwater, and the river of Fisherville Mill Site as shown on Figure 3.4 and analyzed using a variety of techniques. In addition, samples were analyzed for pH, conductivity, dissolved oxygen and temperature. The results are shown in table 4.1.

<table>
<thead>
<tr>
<th>Sample Locations</th>
<th>pH</th>
<th>Dissolved Oxygen (mg/L)</th>
<th>Conductivity in Field (µS)</th>
<th>Field Temperature (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fisherville Canal Location 1</td>
<td>7.09</td>
<td>9.28 (Upstream)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fisherville Canal Location 2</td>
<td>8.77</td>
<td>-</td>
<td>213</td>
<td>28.0</td>
</tr>
<tr>
<td>Fisherville Canal Location 3</td>
<td>8.39</td>
<td>10.57 (Downstream)</td>
<td>194.6</td>
<td>26.7</td>
</tr>
<tr>
<td>Blackstone River</td>
<td>7.66</td>
<td>7.00</td>
<td>179.8</td>
<td>24.9</td>
</tr>
</tbody>
</table>
The surface of the canal is typically covered with a layer containing oily substances that are likely associated with heavy oil leaking from the dam and natural organic matter from surrounding plants. The dissolved oxygen analyses demonstrated that dissolved oxygen is low in the river compared to other samples. The dissolved oxygen values for Locations 2 and 3 on the canal are relatively high. The high dissolved oxygen values in the canal may be associated with algae activity. In addition, pH of the canal is high relative to river. As discussed in the following sections, the fluorometric analyses using the field fluorometer and luminescence spectrophotometer demonstrated that the source of the oily substance is likely related to the oil contamination.

4.2. Modelling Results

A model was developed using contour maps from Woodard & Curran (2008) and model developed by Colar & Colantonio (2003). Using modelling software Visual Modflow Flex developed by Schlumberger (2014) for groundwater flow analysis Fisherville Mill Site groundwater flow heads, transport path of contaminant, source of contamination in observation wells and zone budget was modelled to understand flow of groundwater and transport of contaminant in groundwater.

4.2.1. Numerical Model Groundwater Flow Counters

Models were developed for two cases: one in which the South Grafton Water District (SGWD) water supply wells were not in operation, and a second in which wells were in operation. The SGWD wells are located at south-west of the site. For the first case, the model was developed without operation of SGWD pumping wells that provides water to Grafton. The model was developed demonstrated that groundwater in each layer flows from north (Fisherville Pond) to the southeast (Blackstone River). This flow pattern is shown in figure 4.1 for layer 2, which consists of a mixture of sand & gravel and peat materials. As indicated in this figure the flow of the groundwater in all layers (except for the upper layer where there is no flow) is directed towards Blackstone River due to the regional topography and flow to the river from Blackstone Canal, which is located to the West edge of the site. In addition, the model shows that water from canal flows toward the river and as such transports any associated contaminants to the river.
For the second case, the model was set such that it included the SGWD pumping wells. The results for this case are shown in Figure 4.2. Because of the hydraulic gradient associated with the SGWD pumping wells, the groundwater flows toward pumping wells. However, the primary flow of the groundwater is still directed to the river. This indicates that pumping wells do not have significant effect on the flow of the groundwater. In addition, the zone budget water balance results in Appendix shows that the majority of groundwater flows to the river from canal and a small amount of flow is directed to the pumping wells.
4.2.2. Forward Particle Transport Path Models

The transport of the contamination in groundwater is important because groundwater serves as water supply for the population. Therefore, to determine the pathways and destination of the contaminants in the site, the Modpath features of the model were used to understand the transport pathlines followed by the contaminants. Figure 4.3 shows the pathline of the contaminant transport in groundwater. Four particles were allocated to the spill site and three particles were allocated along the canal where surface water samples were collected. The developed model shows that particles travel toward the river. Figure 4.4 is included to clarify the three dimensional nature of the transport. This figure shows that particles travel primarily through layer 2. However, depending on the start location of the particle, they enter the river either from the first or second layer. Figure 4.5 and 4.6 shows the particle transport with pumping wells included to the model. The developed model for pumping condition (i.e. the case with the SGWD wells in operation) shows that the pumping wells do not affect the overall travel direction of the particles.
Figure 4.3 Forward Particle Transport Model

Figure 4.4 3D Forward Particle Transport Model
Figure 4.5 Forward Particle Transport Model with pumping wells

Figure 4.6 3D Forward Particle Transport Model with pumping wells
4.2.3. Backward Particle Transport Path Models

Several samples were collected from the Fisherville Mill Site and the fluorometric and GC FID analyses showed the presence of the oil contamination. Therefore, to determine the source of the contamination and its travel route, the model particle backtracking feature of the model was developed. Figures 4.7 - 4.10 shows the route of the particle in static condition and figures 4.11 - 4.14 shows with pumping wells operating. The developed transport model demonstrates that contamination source is from north-west of the site but the samples collected from shallow wells travel through second layer and the samples collected from deep wells travel through third layer to the sample collection area. Again, the pumping wells do not affect the transport of the contamination.

Figure 4.7 Backward Particle Transport Model from the location of shallow wells
Figure 4.8 3D Backward Particle Transport Model from the location of shallow wells

Figure 4.9 Backward Particle Transport Model from the location of deep wells
Figure 4.10 3D Backward Particle Transport Model from the location of deep wells

Figure 4.11 Backward Particle Transport Model from the location of shallow wells with pumping wells
Figure 4.12 3D Backward Particle Transport Model from the location of shallow wells with pumping wells

Figure 4.13 Backward Particle Transport Model from the location of deep wells with pumping wells
4.3. Field Fluorometer Results

Samples collected from the canal, groundwater and the river were analyzed using the 10 AU Field Fluorometer for raw fluorescence. To provide a full characterization of the contamination, samples were analyzed using both the short wavelength and long wavelength kits of the field fluorometer. The results of the field fluorometer were intended to determine if the samples contained fluorescing organic matter and if the analyses could provide an indication of the applicability of field fluorometer in characterizing organic contamination. Further analyses using other techniques were also completed to provide detailed characterization of organic matter in water and provide a basis for comparing the effectiveness of the field fluorometer results.

4.3.1. Fluorometer Short Wavelength Results

The Fisherville Mill Site samples were analyzed using the fluorometer with the short wavelength filter set, which includes an excitation spectrum set at 254 nm and emission spectrum set between 300-400 nm. The equivalent concentration (as indicated by NDSA standard) for the
fluorescing organic contaminants were calculated with equation 2. The calculated values of the equivalent concentrations using the calibration curve are shown in figure 4.15 and table 4.2 lists the calculated results.

**Table 4.2** Equivalent concentration of contaminant in Fisherville Mill Site water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration (PPB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater Location 1</td>
<td>116.6</td>
</tr>
<tr>
<td>Groundwater Location 2</td>
<td>87.7</td>
</tr>
<tr>
<td>Groundwater Location 3</td>
<td>33.3</td>
</tr>
<tr>
<td>Groundwater Location 4</td>
<td>40.2</td>
</tr>
<tr>
<td>Blackstone Canal</td>
<td>62</td>
</tr>
<tr>
<td>Fisherville Mill</td>
<td>537.4</td>
</tr>
</tbody>
</table>

**Figure 4.15** Equivalent concentrations of water samples with short wavelength

The calculated equivalent concentration allocated to their respectful locations demonstrates that raw fluorescence of contaminant is higher in the well at location 1 (which is next to Blackstone River and has longest travel time) than the fluorescence in the Blackstone Canal as shown in
Woodard and Curran (2008) mention that groundwater flow in shallow overburden flows faster than deeper portions of the overburden. This may explain the higher concentration of the contaminant in that well. It is also possible that the location 1 is directly on a flowpath that is directly down gradient of the spill site (where the concentration is extremely high).

![Location of equivalent concentrations of water samples](Photo by Eugene Bernat)

**Figure 4.16** Location of equivalent concentrations of water samples (Photo by Eugene Bernat)

### 4.3.2. Fluorometer Long Wavelength Results

The Fisherville Mill Site samples were also analyzed using the fluorometer with a long wavelength filter set that included excitation wavelengths between 300-400 nm and emission wavelengths between 410-600 nm. Equivalent concentrations of the contaminants (as indicated by PTSA) were calculated using equation 4. The calculation of equivalent concentrations using calibration curve is shown on figure 4.17 and table 4.3 lists the calculated results.
Table 4.3 Equivalent concentration of contaminant in Fisherville Mill Site water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Equivalent Concentration (PPB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater Location 1</td>
<td>27</td>
</tr>
<tr>
<td>Groundwater Location 2</td>
<td>11</td>
</tr>
<tr>
<td>Groundwater Location 3</td>
<td>12</td>
</tr>
<tr>
<td>Groundwater Location 4</td>
<td>1.5</td>
</tr>
<tr>
<td>Blackstone Canal</td>
<td>51</td>
</tr>
<tr>
<td>Fisherville Mill</td>
<td>104</td>
</tr>
</tbody>
</table>

Figure 4.17 Equivalent concentrations of water samples with long wavelength

The calculated equivalent concentration for the various locations demonstrates that raw fluorescence of sample is high in the Groundwater 1 (i.e. well adjacent to Blackstone River). The equivalent concentration calculated using the short wavelength kit for the filed fluorometer is also high at this location. Figure 4.18 shows the equivalent concentrations in the wells where samples were collected. The reason for the high concentration of the contaminant in Groundwater 1 adjacent to the river is that the groundwater flows towards the river in a southeasterly direction from the mill and canal as was explained in Section 4.2.1. It is quite likely that Groundwater Location 1 is directly on a flowpath passing through the source area, and
these results are consistent with the backward tracking results in Section 4.2.3. In general, both the short wavelength and long wavelength analysis displayed similar trends, confirming the presence of fluorescing organic material. The results demonstrate that the field fluorometer is as useful tool for identifying the presences of oil contamination in groundwater.

![Figure 4.18 Location of equivalent concentrations of water samples (Photo by Eugene Bernat)](image)

### 4.4. Absorbance Spectrometry Results

The Fisherville samples were analyzed with Shimadzu UV2100U to determine the absorbance spectra range of the organic contaminants. The goal of these analyzes were to provide a better understanding optimal range of absorbance for PAHs, to provide a basis for advanced fluorescence analysis with the fluorescence spectrometer, and also determine if the absorbance spectra can serve as a useful tool for forensics or source tracking.
4.4.1. Absorbance Spectra for the Aromatic Hydrocarbon Standard

First, an aromatic hydrocarbon standard used in GC analyses was used to understand the absorbance of the PAHs. The standard consists of 17 PAHs. Different concentrations of the standard were diluted to assess the differences between absorbance and determine similarity for the various peaks displayed by fluorescent spectra. Figure 4.19 shows that the absorbance is low for wavelengths above 400 nm, and high for wavelengths closer to 200 nm. Absorbance for wavelengths lower 225 nm can be ignored since they appear to be within the range of noise and higher energies are normally found at smaller wavelengths. From the absorbance spectrometry results, PAHs have good absorbance between 225-400 nm and several peaks are seen in that range. Fluorescing materials get to an excited state by absorbing the photons from the light. After getting to excited state fluorescing materials decrease to ground state by emitting the absorbed energy in certain range of wavelengths. This is called fluorescence of the material. Therefore, absorbance spectrum results shown on figure 4.19 can be assumed as the excitation range for PAHs and can be used in fluorescence analyses.

As noted previously, the standard used in this analysis consisted of 17 PAHs and several of these peaks can be identified on the absorbance curve. The current forensic methods for identification of organic contamination sources use certain ratios of compounds found in oil and include consideration of PAHs. Therefore, determining the contribution of the PAHs to the peaks on the absorbance spectra of the aromatic hydrocarbon standard might lead to the application of absorbance spectrometry as forensic method, using the ratios of PAHs as in other forensic techniques (e.g. gas chromatography).
4.4.2. *Absorbance Spectra for the Deep Horizon Spill Crude Oil*

Crude oil is a mixture of complex compounds and the PAHs found in crude oil do not just consist of only 17 PAHs as in the standard; there are actually 50 PAHs identified in crude oil. As such, the complexity of crude oil affects the absorbance spectrum results because the differences between spectra from crude oil and spectra from the aromatic hydrocarbon standard. Therefore, to understand this difference, different concentrations of the BP crude oil were diluted in dichloromethane and analyzed for absorbance. The results of these analyses are shown in figure 4.20. As seen in Figure 4.20, the absorbance spectra for different BP crude oil dilutions do not have clear peaks as was observed for the aromatic hydrocarbon standard. However, a small raised portion of the curve (i.e. a “hump”) is apparent between 250-300 nm and the hump gets more distinct with increasing concentrations of crude oil. As demonstrated in the aromatic hydrocarbon standard results, the majority of the peaks (and highest peaks) are in between 250-300 nm demonstrating the absorbance spectrum range for PAHs in crude oil. However, because of the low intensity of the curve, the absorbance spectrum analyses need to be performed after fractionation of the crude oil to provide the aromatic fraction, which can subsequently be compared with the aromatic hydrocarbon standard.
4.4.3. Absorbance Spectra for the Fisherville Mill Site Water Samples

Because of the interaction and weathering effects of environmental conditions, contamination found in environment due to oil has different constituents of compounds than pure crude oil. The significance of the weathering on these constituents is apparent in Figure 4.21, which shows the absorbance spectrum results for different water samples collected in different locations in Fisherville Mill Site. As seen on Figure 4.21, a curve between 225-300 nm demonstrates absorbance spectrum range for the oil contaminant. The spectral range for the absorbance for some site samples has a similar range as the range of the aromatic hydrocarbon standard and BP crude oil.

The absorbance spectra of water samples can be distinguished from the crude oil absorbance spectra by the sudden drop in the left shoulder of the curve, as compared to crude oil curve that has a gradually decreasing left shoulder. Another difference between the spectra of the water samples and those from crude oil is sample from Fisherville Mill shown in figure 4.19 is that the Fisherville samples have several identifiable peaks. The reason these peaks occur may be that the
source of the sample could be different from the source of the contamination of the rest samples from the site. Woodard & Curran (2008) identified the Fisherville Mill oil contamination in previous site analyses as refined heavy oil with a higher percentage of PAHs compared to other compounds. This difference between samples from same site and different types of oil demonstrates the potential for using of absorbance spectra to differentiate between different oil contamination sources. However, in order to fully understand the effectiveness of absorbance spectrometry methods, more analyses with additional types of oil and different percentages of PAHs are still needed.

![Absorbance Spectrum of water samples from Fisherville Mill Site](image)

**Figure 4.21** Absorbance Spectrum of water samples from Fisherville Mill Site

**4.5. Fluorescence Spectrometry Results**

A Perkin Elmer 50B luminescence spectrophotometer was used to analyze water samples and standards to assess the effectiveness of characterizing oil contamination using this instrument. One goal was to assess the use of the short and long wavelength optical filters (specified for the 10 AU field fluorometer) on characterizing contamination associated with refined and crude oil
in the environment. The analyses included the Fisherville site, standards recommended for use with field fluorometer (i.e. NDSA and PTSA), along with additional analyses crude oil samples and samples collected from Bayou Corne contamination site.

4.5.1. *Fluorescence Spectra for the Aromatic Hydrocarbon Standard*

First, concentrations of a 10 µl of aromatic hydrocarbon standard diluted in dichloromethane (DCM) were scanned to determine the standard’s excitation spectra and emission spectra. The concentrations of the standard were chosen to be similar to concentrations used in GC analyses. Dichloromethane and hexane were used as primary solvents for dissolving organic material to analyze its fluorescence. In addition, dichloromethane was used as an extraction solvent in extraction procedure of this research representing the solvent of prepared samples. The results are shown on figure 4.22. The blue curve shows the excitation spectral range for the 17 PAHs found in the aromatic hydrocarbon standard to be between ~225 and 400 nm, which was similar to the absorbance range found for the absorbance spectrophotometer. This confirms that the fluorometer can be used to determine an absorbance spectrum for the contaminant. For this standard, a range of high intensities for the excitation spectra were found to be between ~225 and 310 nm, which is within the working range for the excitation filters for the short and long wavelength filter kits provided for the field fluorometer.

The spectral range of the emission spectrum for the aromatic hydrocarbon standard has five peaks with two peaks appearing as small curves on the shoulder of the right side of the main curve. The five peaks are more distinct if the aromatic hydrocarbons are diluted in hexane rather than dichloromethane, as shown on figure 4.23. This difference is likely because certain PAHs dissolve in hexane much better than in dichloromethane. The emission spectra of aromatic hydrocarbon standard are between ~350-600 nm with highest peaks ranging between 400-500 nm. This demonstrates that PAHs emit light wavelengths that are more intense in long wavelength filter range rather than in short wavelength filter range. Additional results using fluorescence spectrophotometry with different concentrations of the standard can be found in Appendix 3. The results demonstrated similarity in their spectral range with the only differences resulting from changes in intensity of the spectra.
Figure 4.22 Excitation and emission spectra for a 10 µl Aromatic Hydrocarbon Standard diluted in DCM. (The blue curve is excitation spectrum and red curve is the emission spectrum).

Figure 4.23 Excitation and emission spectra for a 5 µl Aromatic Standard diluted in Hexane. (The blue curve is excitation spectrum and red curve is the emission spectrum).

4.5.2. Fluorescence Spectra for the Deep Horizon Spill Crude Oil

The excitation spectrum for crude oil is shown in figure 4.24. As shown in this figure, the excitation wavelength range for crude oil is between ~225 and 400 nm. The fluorescence
excitation spectrum of crude oil has broader range compared to its absorbance spectrum. However, the highest intensity of excitation is between 225 and 300 nm, which matches the results for the absorbance spectrum. The excitation spectrum of the Deep Horizon Spill crude oil also suggests that the fluorometer short wavelength kit’s excitation filter will have better results in detecting crude oil contamination in the water than the long wavelength kit’s excitation filter. The short wavelength kit’s excitation filter allows light at 254 nm, which is within the highest intensity range for crude oil excitation spectrum. The long wavelength kit’s excitation filter allows light to pass between 300-400 nm, which exceeds the optimal range of excitation spectrum for BP crude oil.

Figure 4.24 also shows the emission spectrum scan for the crude oil. The emission range for the crude oil is between approximately 300 and 550 nm. The emission spectrum for the crude oil has one major peak compared to five distinct peaks that were apparent in the emission spectrum for the aromatic hydrocarbon standard, even though the crude oil has a greater number of PAH compounds. This suggests that PAHs in crude oil emit the light in similar range as the standard, although the crude oil spectrum has one major curve rather than several distinct peaks.

**Figure 4.24** Excitation and emission spectra for a 100 µl of Deep Horizon Spill Crude Oil diluted in DCM. (The blue curve is excitation spectrum and red curve is the emission spectrum).
4.5.3. *Fluorescence Spectra for the Fisherville Mill Site Water Samples*

Figures 4.25, 4.26 and 4.27 show emission spectra with an excitation wavelength of 254 nm for groundwater samples from the Fisherville Mill Site (take from Groundwater Location 2), a surface water sample from Blackstone Canal, and a water sample from the spill area in the Fisherville Mill Site, respectively. The emission spectrum results for groundwater shows two peaks between 350 and 500 nm, although the second peak is difficult to distinguish because the noise level is high and it resembles the extension of the right shoulder of the first curve. The second curve is located between ~425 nm and 500 nm. The peak at 500 nm is the emission from the solvent as shown in figure 3.10. The result is similar is for the water sample from the spill area (Figure 4.27). The surface water sample from Blackstone Canal has two distinct curves that merged together. The contaminant emission spectrum for the Blackstone Canal is different from that of the groundwater and the spill site samples since it has second peak that is slightly higher in intensity than the first peak. This observation can be because the contaminant in the canal is different from the groundwater and the spill area contaminants or have different constituents of PAHs due to weathering of the contaminant.

![Graph showing fluorescence spectra](image-url)

**Figure 4.25** Groundwater Location 2 Emission Spectrum at 254 nm excitation
Figures 4.28, 4.29 and 4.30 show emission spectra with excitations at 325 nm for a groundwater sample from Fisherville Mill Site, a surface water sample from the Blackstone Canal and a water sample from spill area in the Fisherville Mill Site. As for the aromatic hydrocarbon standard emission spectra, two peaks can be distinguished for each sample. These peaks are between 350 and 650 nm for each sample. The two peaks before 350 nm and after 650 nm are emission spectrum from the solvent dichloromethane. Contaminants found in groundwater and canal display similarity in their peaks since both of the contaminants have a smaller first peak.
compared the peaks of the contaminants from spill area. This result likely because the contaminants found in groundwater and in the canal are different from the contaminants in the spill area either due to the source of contamination or by weathering effects of the environment. From the results at excitation 254 nm and 325 nm, it can be concluded that the fluorometer excitation and emission wavelength for both short and long wavelength are demonstrating the expected results. In addition, when comparing the excitation results, the similarity of contaminants in all three locations suggest that the all samples of Fisherville Mill Site are associated with a single source. The results provide a basis for refining the wavelength specifications normally designated for field fluorometers, and also provide a basis for more in-depth analysis of excitation and emission spectra associated with PAH’s.

Figure 4.28 Groundwater Location 2 Emission Spectrum at 325 nm excitation
Figure 4.29 Blackstone Canal water sample Emission Spectrum at 325 nm excitation

Figure 4.30 Fisherville Mill Spill water sample Emission Spectrum at 325 nm excitation

4.6. Gas Chromatography with Flame Ionization Detector Results

Gas chromatography with a flame ionization detector (GC FID) was used to determine the detailed constituents of the contaminants and as well as the origin of the contamination. In these analyses, three different types of samples were analyzed and their chromatographs were compared. These samples were crude oil associated with the Deepwater Horizon Spill, water and
soil samples collected from the Bayou Corne sinkhole site, and surface water and groundwater samples from the Fisherville Mill Site. Prior to completing the analyses, the samples were fractioned to their aliphatic and aromatic fractions and analyzed separately.

4.6.1. Gas Chromatograms of Aliphatic Fraction

By using the extraction and fractionation procedures described in chapter 3, the samples were separated to their aliphatic and aromatic fractions. Figures 4.31, 4.32 and 4.33 show plots of the aliphatic hydrocarbon fractions for the samples. These fractions were identified by comparing the retention time of the peaks on sample chromatographs with the aliphatic hydrocarbon standard’s retention times listed in figure 3.13. In addition, other aliphatic hydrocarbons exist, but these cannot be identified because the aliphatic hydrocarbon standard only includes a limited set of aliphatic hydrocarbons. Using the identified aliphatic hydrocarbons ratios $\Sigma n$-alkanes/n-16 and Low Molecular Weight to High Molecular Weight (LMW/HMW) of BP crude oil and Bayou Corne samples were compared. Using the ratios source of contamination can be identified either petrogenic or biogenic. The results of the ratios for the samples are listed in Table 4.4.

![Figure 4.31 Deep Horizon Spill Crude Oil Identified Aliphatic Fraction](image-url)
Figure 4.32 Bayou Corne sinkhole surface water sample Aliphatic Fraction

Figure 4.33 Bayou Corne sinkhole soil sample Aliphatic Fraction
Table 4.4 Aliphatic Ratio Results

<table>
<thead>
<tr>
<th></th>
<th>Deep Horizon Spill Crude Oil</th>
<th>Bayou Corne Water Sample</th>
<th>Bayou Corne Soil Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sum n$-alkanes/n-16</td>
<td>6.93</td>
<td>4.89</td>
<td>12.52</td>
</tr>
<tr>
<td>LMW/HMW</td>
<td>2.42</td>
<td>1.93</td>
<td>0.51</td>
</tr>
</tbody>
</table>

The Deep Horizon Spill crude oil results show that these ratios can be used to characterize the contaminant. The $\sum n$-alkanes/n-16 ratio of the soil sample from Bayou Corne is higher than ratio for the water sample, but both calculated ratios suggest the presence of oil contamination. This difference may be related to the degree of weathering. It is possible that the oil contaminants in the soil could be more weathered than the contaminants in the water sample, in which case low molecular weight alkanes degrade faster than high molecular weight alkanes. The potential for weathering is also suggested by the small ratio of the LMW/HMW for the soil sample compared to water sample ratio. The water sample has a LMW/HMW ratio close to two, which is indicative of weathered fresh oil while the LMW/HMW ratio for the soil which is lower than 1, which is indicative of either a severely weathered oil or a different oil source.

Figures 4.34 and 4.35 show the aliphatic fraction chromatograms for the water samples that were collected from the Fisherville Mill Site. No aliphatic hydrocarbons can be identified on the chromatograms, which suggests that the either aliphatic hydrocarbons are weathered with low concentrations that are below the detection limit of the GC FID, or that there is no oil contamination. Therefore, PAH analyses are needed to identify source of oil contamination since PAHs exhibit more resistance to weathering than aliphatic hydrocarbons.
4.6.2. **Gas Chromatographs of Aromatic Fraction**

Figures 4.36, 4.37, 4.38, 4.39 and 4.40 show the chromatograms for the aromatic fraction for BP crude oil, Bayou Corne water and soil samples and Fisherville Mill Site water and groundwater samples. There are no identified peaks of PAHs on chromatogram, which suggests that method used for fractionation performed poorly to separate PAHs from unresolved complex mixture (UCM). The extraction method performed well compared to fractionation since hydrocarbons were extracted from water and soil matrices as seen for both aliphatic and aromatic hydrocarbon chromatograms. Regardless of the absence of PAH peaks, the UCM can be used to determine the source of the contamination and level of weathering of the oil contaminant (Wang and Fingas, 2003).
The chromatogram for the Deep Horizon Spill crude oil aromatic fraction in Figure 4.36 shows a small rise of UCM, which suggests that the oil is not weathered, which would be expected since this sample is a pure form of crude oil and was not exposed to environmental conditions other than during it is extraction from the ground.

Conversely, aromatic chromatograms of samples from the Bayou Corne and Fisherville Mill Site (Figures 4.37 and 4.39) have trends that more distinct in UCM. First, for Bayou Corne, the samples have UCM with two distinct rises, compared to the samples from the Fisherville Mill Site, which have only rise in the one UCM. The structure of Bayou Corne samples UCM suggests that both water and soil samples have a similar source of contamination, since the UCM is the least affected by weathering conditions. In addition, the structure of UCM chromatogram for both samples suggests that source of oil contamination is crude oil since the increase in UCM of the Bayou Corne samples shows up at the middle and end of the retention time. The UCM also shows up in chromatograms for the aliphatic fraction of the samples, which suggests that Bayou Corne samples have more complicated contamination requiring a higher quality of fractionation method.

The results for surface water and groundwater samples collected at the Fisherville Mill Site (Figures 4.39 and 4.40) also have similar characteristics, indicating that these samples also have the same contamination source. In addition, the UCM peak showing up at the final minutes of chromatogram likely indicates that the oil contaminant is refined oil, which consists of heavy molecular weight hydrocarbons (e.g. heavy fuel oil). In general, similar trends in UCM for the source and groundwater samples at the Fisherville Site confirm the relationship between the contaminations at the two locations.
**Figure 4.36** GC-FID chromatograph of Aromatic Fraction of the Deep Horizon Spill Crude Oil

**Figure 4.37** GC-FID chromatograph of Aromatic Fraction of the Bayou Corne sinkhole surface water sample

**Figure 4.38** GC-FID chromatograph of Aromatic Fraction of the Bayou Corne sinkhole surface water sample
**Figure 4.39** GC-FID chromatograph of Aromatic Fraction of the Fisherville Mille Site groundwater

**Figure 4.40** GC-FID chromatograph of Aromatic Fraction of the Fisherville Mille Site spill water sample
5. SUMMARY AND CONCLUSION

This research evaluated the effectiveness of fluorometric techniques in characterizing the transport of polycyclic aromatic hydrocarbons (PAHs) associated with petroleum hydrocarbons in the environment. Samples from contaminated sites were analyzed using different fluorometric techniques, including raw fluorescence absorbance, absorbance spectra, fluorescence spectra, and gas chromatography to determine the nature of the detailed constituents of the contaminants. The analyses were completed to characterize the distribution of results demonstrated the usefulness of the fluorometric techniques for source tracking and understanding the transport of organic contaminants.

The field site at Fisherville Pond provided the opportunity to use fluorometric techniques to characterize distribution of the contamination due to PAHs at the site. A groundwater flow model was developed and particle tracking was used to understand the flow of the groundwater and pathways associated with the contaminant transport.

The groundwater model demonstrated that water flows from the north (Fisherville Pond) region of the site to the southeast towards Blackstone River. It was found that the flow of the groundwater is not affected by pumping wells and follows regional topography (elevations of the surface layer), flowing from Blackstone Canal to the river. In addition, the model showed that water from canal flows toward the river and as such, any associated contaminants are transported towards the Blackstone River. The particle backtracking demonstrated that the primary source of the contamination in the wells where samples were collected for analyses is Blackstone Canal. The flow and particle tracking results provided a context for analyzing and comparing the various analyses of the samples.

The results from field fluorometer were consistent with the results from the particle tracking and provided information for presence of fluorescing material in the groundwater. The equivalent concentration of the contaminant calculated from the calibration curve of the short wavelength kit demonstrated to be higher in value than to the equivalent concentration calculated from the calibration curve of long wavelength. Nevertheless, both wavelength kits were able to detect oil contamination in water samples from the Fisherville Mill Site. In addition, to the analyses that
assessed the effectiveness of the short and long wavelength kits, the fluorometer results provided with the basic information on the spectral range for absorbance and fluorescence analyses. Further analyses of the groundwater samples with other techniques demonstrated usefulness of the field fluorometer on detecting oil contamination.

Comparison of the absorbance spectra of aromatic hydrocarbon standard, Deep Horizon Spill crude oil and Fisherville water samples revealed that the absorbance spectra for all samples were in the range of approximately 250 nm and 300 nm. For this case, this spectral range is likely an appropriate absorbance range for the polycyclic aromatic hydrocarbons (PAHs) regardless of their source. In addition, standard absorbance spectra and Fisherville water sample results demonstrated several distinct peaks in similar wavelength ranges, suggesting the possibility of using absorbance spectrometry as forensic method for oil source determination.

Fluorescence spectral analyses of the aromatic hydrocarbon standard, Deep Horizon Spill crude oil and Fisherville water samples revealed similarities between spectral ranges of the absorbance and excitation spectra. Excitation spectrum results for the Deep Horizon Spill crude oil suggest that the excitation filter for the short wavelength kit of the field fluorometer will have better results than excitation filter for the long wavelength kit when detecting crude oil contamination in the water. The excitation and emission spectrum results for Fisherville Mill Site revealed that the fluorometer excitation and emission wavelength for both short and long wavelength are demonstrating the expected results. In addition, when comparing the excitation results, the similarity of contaminants in all three locations suggest that the all samples of Fisherville Mill Site are associated with a single source.

Gas chromatography with a flame ionization detector (GC FID) was used to gain a better understanding of the nature of the contaminants in the aliphatic and aromatic fractions of the samples. Analyses were completed for crude oil associated with the Deepwater Horizon Spill, water and soil samples collected from the Bayou Corne sinkhole site, and surface water and groundwater samples from the Fisherville Mill Site. First, for the Bayou Corne site, both water and soil sample were analyzed. Since the constituents of the water and soil samples were found to be different, common ratios were used to analyze the results. The $\Sigma n$-alkanes/$n$-16 ratio of the soil sample from Bayou Corne was found to be higher than the ratio for the water sample, but
both calculated ratios suggest the presence of oil contamination. This difference may be related to the degree of weathering. It is possible that the oil contaminants in the soil could be more weathered than the contaminants in the water sample. This was also suggested by the small ratio of LMW/HMW of the soil sample as compared to water sample ratio. The water sample has a LMW/HMW ratio close to two, which is indicative of weathered fresh oil while the LMW/HMW ratio for the soil is lower than one, which is indicative of either severely weathered oil or a different oil source. The effectiveness of the ratios \( \sum n\text{-alkanes}/n\text{-16} \) and LMW/HMW were also tested using pure crude oil. The results were successful in demonstrating that the oil was fresh crude oil.

In the gas chromatographs of Fisherville Mill Site samples, no aliphatic hydrocarbons could be identified on the chromatograms, which suggests that the either aliphatic hydrocarbons are weathered with low concentrations that are below the detection limit of the GC FID, or that there is no oil contamination. Given variety of results that confirm the presence of organics (and the fact that these results are consistent with previous results), it likely the aliphatics are below detection limits. Since PAHs exhibit more resistance to weathering than aliphatic hydrocarbons, PAH analyses were performed to identify source of oil contamination. However, when reviewing the peaks of the chromatographs for the PAHs, no peaks could be identified. This result suggests that method used for fractionation performed poorly when separating the PAHs from any unresolved complex mixture (UCM) that is present. The extraction method performed well compared to fractionation since hydrocarbons were extracted from water and soil matrices as seen for both aliphatic and aromatic hydrocarbon chromatograms for Bayou Corne and BP crude oil. Regardless of the absence of PAH peaks, it was found that the UCM was helpful in determining the source of the contamination and level of weathering of the oil contaminant.

The structure of the UCM for the Bayou Corne samples demonstrates that both water and soil samples have a similar source of contamination, since UCM is the least affected by weathering conditions. In addition, the structure of UCM chromatogram for both samples indicates that source of oil contamination is crude oil since the UCM of the Bayou Corne samples appeared at the middle and end of retention time. The UCM also showed up in chromatograms for the aliphatic fraction of the samples, which suggests that Bayou Corne samples have more complicated contamination.
The gas chromatography results for surface water and groundwater samples collected at the Fisherville Mill Site also have similar UCM characteristics, indicating that these samples have the same contamination source as well. In addition, the presence of a UCM peak, which showed up in the final minutes of chromatogram likely indicates that the oil contaminant is refined oil, consisting of heavy molecular weight hydrocarbons (e.g. heavy fuel oil).

From the above results, it can be concluded that the methods used in this research performed well and can be used depending on type of the investigation or research performed. Nevertheless, some difficulties remain, and it is important to recognize that the fluorometric techniques can be improved even more. Therefore, the following suggestions are recommended as next steps in the analysis of fluorescence techniques for characterizing PAHs and organics:

- The characteristics of the absorbance spectrum should be determined for each PAH and compared to absorbance results of aromatic hydrocarbon standard.
- An absorbance spectrum analyses for crude oil should be performed after it has fractionated to its aromatics. In addition, comparisons of absorbance spectra for different crude oil types can give insight on effectiveness of absorbance spectrometry.
- The fluorescence emission spectrum results for all samples demonstrated the high intensity between 400-410 nm. Therefore, this wavelength range should be included either to the short wavelength kit or to long wavelength kit of the 10 AU field fluorometer.
- The analyses with Bayou Corne provide some insight into the nature of GC FID analyses for a complex organic. However, it is recognized that samples with complex contamination such as Bayou Corne likely require more advanced extraction and fractionation methods compared than to the methods used in this research.

In general, it was found that fluorescence techniques offer excellent opportunities for characterizing organic contamination. To further develop these opportunities, the following research avenues should be considered:

- Determine the factors affecting the absorbance spectra of the PAHs in crude oil.
- Determine the factors affecting the fluorescence spectra of the PAHs in crude oil.
• Gain a better understanding of the interpretation of the absorbance and fluorescence peaks of aromatic hydrocarbon standards and crude oils.
• Determine the effectiveness of absorbance and fluorescence spectrophotometry techniques in distinguishing between biogenic, petrogenic and pyrogenic PAH sources.

By exploring some of these options, the use of fluorescence can be further developed to provide an effective approach for characterizing the subsurface.
REFERENCES


Woodard & Curran, “*Phase II Comprehensive Site Assessment Addendum Report*”, Project No. 210584, 2008


Turner Designs, “*Technical Note: Information for Using NDSA as a Lab Standard for Calibrating Instrumentation*”

Turner Designs, “*Technical Note: Information for Using PTSA as a Lab Standard for Calibrating Instrumentation*”


Coler & Colantonio, Inc., “*Groundwater Flow Model Fisherville Mill Site South Grafton Water District*” 2003
APPENDIX 1 – 10 AU Field Fluorometer Calibration Procedure (Adapted from Turner Designs, 1999)

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Notes &amp; Instructions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Turn on the fluorometer and allow it to warm up for 10 minutes.</td>
<td></td>
</tr>
<tr>
<td>2. Prepare a Standard that is approximately 80% of the highest concentration you want to read, but <strong>still within</strong> the linear range.</td>
<td>See the discussion of broad range, low, and high concentrations above; and Section 3D, screen 2.3.</td>
</tr>
<tr>
<td>3. Have on hand your Blank solution.</td>
<td>See the discussion in Section 3C, screen 2.11; and Section 3E3 on high blank.</td>
</tr>
<tr>
<td>4. Have on hand the samples you wish to read, with any preparation already completed.</td>
<td></td>
</tr>
<tr>
<td>5. Access the Calibration menu, screen 2.0.</td>
<td>From the HOME screen, press &lt;ENT&gt; for the Main Menu, then &lt;2&gt; for screen 2.0.</td>
</tr>
<tr>
<td>6. Set the concentration range control to AUTO.</td>
<td>From screen 2.0, press &lt;4&gt; to bring up screen 2.4, then &lt;3&gt; to bring up screen 2.43 (set conc. control range), and press &lt;ENT&gt; to toggle.</td>
</tr>
<tr>
<td>7. Enter the <strong>actual concentration</strong> for your standard. I.e., 45, 100, 500, etc. (This number must be less than 1000.)</td>
<td>From screen 2.0, press &lt;2&gt; to access screen 2.2 (standard solution value). If you are reading raw fluorescence (set on screen 1.21), then set the standard solution concentration on screen 2.2 to .1, 1, or 10, with 1 preferred. The purpose of this is to allow you to read the Screen 2.3 table as a simple ratio of 10.</td>
</tr>
<tr>
<td>8. If you want the instrument to subtract Blank, make sure screen 2.12 is set to YES.</td>
<td>From screen 2.0, press &lt;1&gt; to access screen 2.1, and make sure subtract blank on screen 2.12 is set to &quot;YES&quot;. See definition under Section 3C, screen 2.11.</td>
</tr>
<tr>
<td>Procedure</td>
<td>Notes &amp; Instructions</td>
</tr>
<tr>
<td>----------------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td><strong>9A. RUN BLANK:</strong></td>
<td>Press &lt;HOME&gt;. While on the HOME screen, insert your Blank (insert a clean, dry on the outside, cuvette containing your blank). Replace the light cap if running discrete samples. <strong>WAIT</strong> about 10 seconds while the instrument determines the correct range. (Lower range is preferred.)</td>
</tr>
<tr>
<td>Determine range to run blank.</td>
<td></td>
</tr>
<tr>
<td><strong>9B. Access Run Blank screen 2.11.</strong></td>
<td>Then, access screen 2.11 by pressing &lt;ENT&gt;, &lt;2&gt;, &lt;1&gt;, and &lt;1&gt;. IF YOU WISH TO ABORT this procedure and revert to the former calibration settings, then press &lt;ESC&gt; before pressing &lt;0&gt;. This will retain the current settings for the Span and Blank.</td>
</tr>
<tr>
<td><strong>9C. While on 2.11, wait until the reading is stable.</strong> Then, if the Blank% (in the center of the screen) is less than 200%, press &lt;0&gt;. If not, reduce the Span by pressing the down arrow until the Blank% is less than 200%. Wait for stable reading, then press &lt;0&gt; to accept the value.</td>
<td>If Blank readings are very high, verify that your Blank is not contaminated. Refer to section E3 above for an alternate method for high Blank. Consider readjusting the basic operating level (Appendix 6B).</td>
</tr>
<tr>
<td><strong>9D. Remove the cuvette and set aside.</strong></td>
<td></td>
</tr>
<tr>
<td><strong>10A. RUN STANDARD:</strong></td>
<td>Press &lt;HOME&gt;. While on the HOME screen, insert your Standard (insert a clean, dry on the outside, cuvette containing your Standard). Replace the light cap if running discrete samples. <strong>WAIT</strong> about 10 seconds while the instrument determines the correct range.</td>
</tr>
<tr>
<td>Determine range to run standard.</td>
<td></td>
</tr>
<tr>
<td>Procedure</td>
<td>Notes &amp; Instructions</td>
</tr>
<tr>
<td>-----------</td>
<td>----------------------</td>
</tr>
<tr>
<td>10B. Access Run Standard Screen 2.3.</td>
<td>From HOME, press &lt;ENT&gt;, &lt;2&gt;, and &lt;3&gt;. Pressing &lt;ESC&gt; before pressing &lt;*&gt; WILL ABORT the standard run and retain the current settings for the Standard.</td>
</tr>
<tr>
<td>10C. To Run Standard, wait until the readings are stable (TC cycles from 1 to 8 seconds when arrows are pressed), then press &lt;*&gt; to accept the values.</td>
<td>Though it is not necessary, you may adjust the Span using the up and down arrows until the FS table readings for the ranges are satisfactory. <strong>NOTE:</strong> Changing the Span on this screen will also affect the Blank % as set on screen 2.11; it is not necessary to re-run Blank. Remember, FS is the maximum concentration or relative fluorescence you will be able to read on a particular range, and it is not necessary or likely that FS match the &quot;value&quot; of the standard.</td>
</tr>
<tr>
<td>10D. Notes about Run Standard Screen 2.3</td>
<td><strong>RAW DATA.</strong> If you are interested in raw fluorescence data, the table readings will indicate the maximum relative fluorescence you can read on each range. I.e., if you entered &quot;1&quot; in step 2 and the reading is 9 on the MED range, you can read a sample 9 times as concentrated as your standard. <strong>NOTE</strong> that the recommendations of when to go to a different calibration method apply here as well.</td>
</tr>
<tr>
<td></td>
<td><strong>BLK&gt;FS.</strong> This indicates that the blank is higher than full scale at this range. This is acceptable if blank is high and you want to read high concentrations, if the FS on the higher ranges is acceptable.</td>
</tr>
<tr>
<td></td>
<td><strong>OVER.</strong> If you calibrate in manual vs. autorange, it is possible that the FS will read OVER. If the FS reads OVER, with the Span close to 0%, it means that the standard concentration is too high for the range you are in. If you are in the LOW range, change to the MED range; if you are in the MED range, change to the HIGH range. To change ranges, &lt;ESC&gt; from screen 2.3. Then, from screen 2.0, press &lt;*&gt; to toggle to the desired range. Then, run step 10.</td>
</tr>
<tr>
<td>Procedure</td>
<td>Notes &amp; Instructions</td>
</tr>
<tr>
<td>--------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>10D. Notes about Run Standard Screen 2.3 (continued)</td>
<td><strong>OVER on the HIGH range.</strong> If you are in the HIGH range and FS reads OVER, with the Span close to 0%, it means the concentration exceeds the maximum limit of detectability for the instrument. Reset the basic operating level (Appendix 6B); consider changing reference filters, or to a smaller cuvette size, or adding an attenuator plate. (See the discussion on decreasing sensitivity in Appendix 6A.)</td>
</tr>
<tr>
<td></td>
<td><strong>&gt;9999.</strong> If FS reading exceeds 9999.999, the maximum allowable for the table, the reading will display &quot;&gt;9999&quot;. To get an on-scale reading, press &lt;ESC&gt; and reduce the standard solution concentration on screen 2.2 by a factor of 10. I.e., if it was 500, set it to 50, or 5 if necessary. If you do this, make note of the factor, as all of your samples will have to be multiplied by this factor to determine the actual concentration. Then, repeat step 10.</td>
</tr>
<tr>
<td></td>
<td><strong>Span equals 99% in the LOW range.</strong> If the Span is 99% and the reading for the LOW range is greater than 10 times the standard solution as set on screen 2.2, it probably means you will not be able to detect concentrations much less concentrated than your standard. (See discussion on increasing sensitivity in Appendix 6A.)</td>
</tr>
</tbody>
</table>
APPENDIX 2 – Gas Chromatograms

Figure A1. BP Crude Oil Aliphatic Fraction

Figure A2. Bayou Corne Water Sample Aliphatic Fraction

Figure A3. Bayou Corne Soil Sample Aliphatic Fraction
Figure A4. 5-α-andorstane

Figure A5. o-terphenyl
Figure A6. 10 µl Aliphatic Hydrocarbon Standard

Figure A7. 25 µl Aliphatic Hydrocarbon Standard

Figure A8. 50 µl Aliphatic Hydrocarbon Standard
Figure A9. 10 µl Aromatic Hydrocarbon Standard

Figure A9. 25 µl Aromatic Hydrocarbon Standard

Figure A9. 50 µl Aromatic Hydrocarbon Standard
APPENDIX 3 – Fluorescence Spectrometry Results

10 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 254 nm

10 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 300 nm

10 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 325 nm

10 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 350 nm
10 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 375 nm

10 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 400 nm

10 microliter Aromatic Standard diluted in 30 ml DCM
Excitation Scan (Blue) 300-400 nm max excitation is 300 nm
Emission Scan (Red) 410-600 nm max emission is 433.1 nm

10 microliter Aromatic Standard diluted in 30 ml DCM
Excitation Scan (Blue) 200-800 nm max excitation is 244 nm
Emission Scan (Red) 200-800 nm max emission is 410 nm
25 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 254 nm

25 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 300 nm

25 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 325 nm

25 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 350 nm
<table>
<thead>
<tr>
<th>25 microliter Aromatic Standard diluted in 30 ml DCM</th>
<th>25 microliter Aromatic Standard diluted in 30 ml DCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excitation 375 nm</td>
<td>Excitation 400 nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>25 microliter Aromatic Standard diluted in 30 ml DCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excitation Scan (Blue) 300-400 nm max excitation is 300 nm</td>
</tr>
<tr>
<td>Emission Scan (Red) 410-600 nm max emission is 434.9 nm</td>
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</table>

<table>
<thead>
<tr>
<th>25 microliter Aromatic Standard diluted in 30 ml DCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excitation Scan (Blue) 200-800 nm max excitation is 239.7 nm</td>
</tr>
<tr>
<td>Emission Scan (Red) 200-800 nm max emission is 408.6 nm</td>
</tr>
</tbody>
</table>
50 microliter Aromatic Standard diluted in 30 ml DCM

Excitation 254 nm

50 microliter Aromatic Standard diluted in 30 ml DCM

Excitation 300 nm

50 microliter Aromatic Standard diluted in 30 ml DCM

Excitation 325 nm

50 microliter Aromatic Standard diluted in 30 ml DCM

Excitation 350 nm
50 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 375 nm

50 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 400 nm

50 microliter Aromatic Standard diluted in 30 ml DCM
Excitation Scan (Blue) 300-400 nm max excitation is 305.5 nm
Emission Scan (Red) 410-600 nm max emission is 435.4 nm

50 microliter Aromatic Standard diluted in 30 ml DCM
Excitation Scan (Blue) 200-800 nm max excitation is 202.3 nm
Emission Scan (Red) 200-800 nm max emission is 407.6 nm

75 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 254 nm

75 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 300 nm
75 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 325 nm

75 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 350 nm

75 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 375 nm

75 microliter Aromatic Standard diluted in 30 ml DCM
Excitation 400 nm
<table>
<thead>
<tr>
<th>ml DCM</th>
<th>DCM</th>
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</thead>
<tbody>
<tr>
<td>Excitation Scan (Blue) 300-400 nm max excitation is 306.6 nm</td>
<td>Excitation Scan (Blue) 200-800 nm max excitation is 205.4 nm</td>
</tr>
<tr>
<td>Emission Scan (Red) 410-600 nm max emission is 433.6 nm</td>
<td>Emission Scan (Red) 200-800 nm max emission is 409.6 nm</td>
</tr>
</tbody>
</table>

100 microliter Aromatic Standard diluted in 30 ml DCM

Excitation 254 nm

Excitation 300 nm

100 microliter Aromatic Standard diluted in 30 ml DCM

Excitation 254 nm

Excitation 300 nm

100 microliter Aromatic Standard diluted in 30 ml DCM
<table>
<thead>
<tr>
<th>Excitation 325 nm</th>
<th>Excitation 350 nm</th>
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<td><img src="image1.png" alt="Graph" /></td>
<td><img src="image2.png" alt="Graph" /></td>
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<tr>
<td><strong>100 microliter Aromatic Standard diluted in 30 ml</strong></td>
<td><strong>100 microliter Aromatic Standard diluted in 30 ml</strong></td>
</tr>
<tr>
<td><strong>DCM</strong></td>
<td><strong>DCM</strong></td>
</tr>
<tr>
<td><strong>Excitation 375 nm</strong></td>
<td><strong>Excitation 400 nm</strong></td>
</tr>
<tr>
<td><img src="image3.png" alt="Graph" /></td>
<td><img src="image4.png" alt="Graph" /></td>
</tr>
<tr>
<td><strong>100 microliter Aromatic Standard diluted in 30 ml</strong></td>
<td><strong>100 microliter Aromatic Standard diluted in 30 ml</strong></td>
</tr>
<tr>
<td><strong>DCM</strong></td>
<td><strong>DCM</strong></td>
</tr>
<tr>
<td><strong>Excitation Scan (Blue) 300-400 nm max excitation is</strong></td>
<td><strong>Excitation Scan (Blue) 200-800 nm max excitation is</strong></td>
</tr>
<tr>
<td>306 nm</td>
<td>202.3 nm</td>
</tr>
<tr>
<td><strong>Emission Scan (Red) 410-600 nm max emission is</strong></td>
<td><strong>Emission Scan (Red) 200-800 nm max emission is</strong></td>
</tr>
<tr>
<td>435.7 nm</td>
<td>409.6 nm</td>
</tr>
</tbody>
</table>
GW1 diluted in 30 ml DCM
Excitation 254 nm

GW1 diluted in 30 ml DCM
Excitation 300 nm

GW1 diluted in 30 ml DCM
Excitation 325 nm

GW1 diluted in 30 ml DCM
Excitation 350 nm

GW1 diluted in 30 ml DCM

GW1 diluted in 30 ml DCM

GW1 diluted in 30 ml DCM

GW1 diluted in 30 ml DCM

GW1 diluted in 30 ml DCM

GW1 diluted in 30 ml DCM

GW1 diluted in 30 ml DCM
<table>
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<td>375 nm</td>
<td>GW1 diluted in 30 ml DCM</td>
</tr>
<tr>
<td>Excitation 400 nm</td>
<td>GW1 diluted in 30 ml DCM</td>
</tr>
<tr>
<td>254 nm</td>
<td>GW2 diluted in 30 ml DCM</td>
</tr>
<tr>
<td>Excitation 300 nm</td>
<td>GW2 diluted in 30 ml DCM</td>
</tr>
<tr>
<td>325 nm</td>
<td>GW2 diluted in 30 ml DCM</td>
</tr>
<tr>
<td>350 nm</td>
<td>GW2 diluted in 30 ml DCM</td>
</tr>
</tbody>
</table>

**GW2 diluted in 30 ml DCM**

- Excitation 254 nm
- Excitation 300 nm
- Excitation 325 nm
- Excitation 350 nm
GW2 diluted in 30 ml DCM
Excitation 375 nm

GW2 diluted in 30 ml DCM
Excitation 400 nm

SW2 diluted in 30 ml DCM
Excitation 254 nm

SW2 diluted in 30 ml DCM
Excitation 300 nm
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Excitation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW2</td>
<td>DCM</td>
<td>325</td>
</tr>
<tr>
<td></td>
<td></td>
<td>350</td>
</tr>
<tr>
<td></td>
<td></td>
<td>375</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
</tr>
<tr>
<td>RW</td>
<td>DCM</td>
<td>254</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
</tr>
</tbody>
</table>

### UV-Vis Spectra

- **SW2 diluted in 30 ml DCM**
  - Excitation 325 nm
  - Excitation 350 nm
  - Excitation 375 nm
  - Excitation 400 nm

- **RW diluted in 30 ml DCM**
  - Excitation 254 nm
  - Excitation 300 nm
RW diluted in 30 ml DCM
Excitation 325 nm

RW diluted in 30 ml DCM
Excitation 350 nm

RW diluted in 30 ml DCM
Excitation 375 nm

RW diluted in 30 ml DCM
Excitation 400 nm
Excitation 375 nm

Excitation 400 nm

Methylene Chloride

Excitation 254 nm

Methylene Chloride

Excitation 300 nm

Methylene Chloride

Excitation 325 nm

Methylene Chloride

Excitation 350 nm
Hexane
Excitation 375 nm

Hexane
Excitation 400 nm
APPENDIX 4 – Modelling Results

Figure A1. Layer 1 Static Condition Groundwater Heads

Figure A2. Layer 3 Static Condition Groundwater Heads
Figure A3. Layer 4 Static Condition Groundwater Heads

Figure A4. Layer 1 Pumping Condition Groundwater Heads
Figure A5. Layer 3 Pumping Condition Groundwater Heads

Figure A6. Layer 4 Pumping Condition Groundwater Heads
Figure A11. Zone Budget Mass Balance in Static Condition

Figure A12. Zone Budget Mass Balance in Pumping Condition