Detection of Oil in Water
Column: Sensor Design

Distribution Statement A: Approved for public release; distribution is unlimited.

February 2013
NOTICE

This document is disseminated under the sponsorship of the Department of Homeland Security in the interest of information exchange. The United States Government assumes no liability for its contents or use thereof.

The United States Government does not endorse products or manufacturers. Trade or manufacturers’ names appear herein solely because they are considered essential to the object of this report.

This report does not constitute a standard, specification, or regulation.

Mr. James E. Fletcher
Environment & Waterways Branch Chief
United States Coast Guard
Research & Development Center
1 Chelsea Street
New London, CT 06320
This report summarizes the results of Phase I (Design Concept) of an RDC effort to develop a readily deployable system for the in-situ detection, identification, and characterization of submerged oil in the water column. The first phase of the project involves development and testing of three technological approaches to the detection problem. A system developed by NORBIT US Ltd. addresses the detection of hydrocarbons using the backscatter from acoustic signals from a Wide Band Multi-Beam Sonar (WBMS). A system developed by WET Labs, named the Fluorescent IN-situ Detection System for OIL (FINDS OIL), uses flow-through fluorometric measurements and fluorescent backscatter to identify and characterize petroleum hydrocarbons encountered by the instrument. A third system, also by Wet Labs, named Wide-angle-scattering Inversion to Detect Oil in Water (WINDOW), uses the scattering and refraction of light to determine the mass and volume concentration, droplet size and density of the entrained oil.

The systems are described in terms of the basic technology, ability to detect and characterize oil, areal coverage, ease of data processing and display, ruggedness and deployability, as well as the challenges involved in preparing the system for Prototype Development and Testing. This report will be used to make a decision on whether to move forward with prototype development for each system.
(This page intentionally left blank.)
Detection of Oil in Water Column: Sensor Design

EXECUTIVE SUMMARY

The U.S. Coast Guard Research and Development Center (RDC) is undertaking an R&D effort to identify and/or develop a system that can detect and characterize oil plumes in the water column. This report summarizes the results of Phase I (Concept Design) of the effort in which remote sensing technology developers were solicited through a Broad Agency Announcement (BAA) to configure and describe systems that were at least at the proof-of-concept stage of development that could potentially address the remote sensing of oil in the water column. This effort is a part of the overall Research and Development (R&D) effort to advance response technology for varying types of oil spills. This subtask addressing entrained oil is similar in scope and objective to an ongoing effort to detect, identify, and characterize oil resting on the bottom (Hansen et al., 2009).

In the BAA, vendors were directed to address a number of capabilities and attributes in describing and conducting preliminary laboratory testing of their concepts. Two vendors proposing three separate systems successfully responded to the BAA, completed the Concept Design phase, and provided final reports describing their efforts. The individual reports included descriptions for each system’s fundamental technologies, system components, remote sensing capabilities, data flow and processing schemes, durability and deployability. The reports also provided proposed technical approaches for additional prototype developments and testing in a simulated oil spill environment such as the Ohmsett facility in Leonardo, NJ. The purpose of this report is to summarize the results of the Phase I activities as reported by the vendors to allow comparison of the results by Coast Guard R&D Program Managers. No attempt is made to critically analyze or corroborate the results, although the relevance of specific findings to follow-on development activities and solving the overall submerged oil response problem is noted.

The systems proposed included one acoustic system and two optical systems. The first system developed by NORBIT US Ltd. addresses the detection of hydrocarbons using the backscatter from acoustic signals from a Wide Band Multi-Beam Sonar (WBMS) at a nominal operating frequency of 400 kHz. The WBMS is a complete, functional system readily deployable on an AUV, ROV, or tow sled. The ultra wide band-width (160 Hz) allows for detection of a wide range of particles (e.g. air bubbles or oil droplets) in the water column. It is relatively lightweight and compact and has moderate power consumption. Its ability to detect plumes of fresh water and dispersed oil were both tested during the proof of concept phase. In both cases the system identified an acoustic anomaly associated with the entrained substance. Further development is needed to resolve false positives in detection by improving software to conclusively identify oil in real-time without subjective analysis of imagery by the operator. The system is deemed ready for follow-on testing at the Ohmsett facility despite concerns regarding interference caused by acoustic reflections from the bottom and walls of the tank.

The second system developed by WET Labs, named the Fluorescent IN-situ Detection System for OIL (FINDS OIL), uses flow-through fluorometric measurements as a primary means of detection and fluorescent backscatter to identify and characterize petroleum hydrocarbons encountered by the instrument. The detection occurs when seawater is passed through a fluorometer and its fluorescence intensity is measured at various wavelengths to identify the type and concentration of petroleum hydrocarbon encountered. From these measurements it is also possible to estimate the density of the oil and dispersant-to-oil ratio. The technology is proven and has been utilized in other systems used to detect and sample hydrocarbon plumes (Li et al., 2011). The drawback with this approach is the limited volume sampled and the uncertainty as to how extensive the hydrocarbon contamination may be in the section of water column...
Detection of Oil in Water Column: Sensor Design

the instrument is sampling. WET Labs proposes to resolve this uncertainty with a second fluorescence backscatter sensor which will scan and detect hydrocarbons in the water volume mixed in the wake of the sampling vehicle (e.g. towed body or AUV). The second sensor would serve as confirmation of the presence of hydrocarbons in the larger volume sampled. The combination of the two sensors will provide identification and characterization of the oil along with estimates of the areal extent of the contamination. The data processing, transmission and display scheme appears straightforward using readily available software, hardware and telemetry systems. Further development initiatives proposed include refinements to the multichannel WETStar fluorescence sensor, integration of sensors into the towed vehicle, testing of the towed vehicle for deployability and maneuverability, refinement of data processing algorithms and database development, and integration of data transmission and display systems. There is concern with system fouling in regions of heavy oil contamination. With respect to testing at the Ohmsett facility, the developers expressed concern about maintaining consistency of oil concentration and distribution in a test plume in the Ohmsett tank, and suggested that a smaller test tank where replication of conditions was more achievable might be better suited for testing hydrocarbon detection and characterization capabilities. They also suggested that tests of deployability and maneuverability were better addressed in open water testing.

A third system, also by WET Labs, named Wide-angle-scattering Inversion to Detect Oil in Water (WINDOW), uses the reflection and refraction of light by suspended oil droplets to determine the mass and volume concentration, droplet size and density of the entrained oil. The wide-angle light scattering (WALS) technique is best suited to detecting and characterizing spherical particles such as air bubbles or oil droplets. As the scattering signatures of oil droplets are collected, they are run through the inversion algorithm to determine their emulsion size distribution, density and viscosity. The instrument is mounted in a hand-deployable probe which is connected to a surface deck unit containing a laptop computer and integrated Global Positioning System (GPS). The information on the extent and properties of the mapped oil plume is disseminated in the form of jpeg images through a wireless network. The system is compact, rugged and deployable by a single individual. Preliminary proof-of-concept testing in the lab showed the system is capable of detecting suspended oil droplets and quantifying their concentration, size distribution and density. As with the previous system, there is some concern with potential fouling of the optical window in heavy oil. Further development activities in preparation for Phase II would focus on inversion algorithm enhancement. There is some concern with respect to the system’s ability to detect and characterize oil that may be aggregated with other marine materials (hence becoming non-spherical in shape and exhibiting unexpected scattering signatures). The system can be easily configured for Phase II testing at the Ohmsett facility.

Specific capabilities of each system with respect to each of the eighteen performance criteria in the BAA are summarized in a table in Section 2.5 of this report. An overall assessment of the current capabilities of each system and potential for further development and testing is provided in Section 3.0.
TABLE OF CONTENTS

EXECUTIVE SUMMARY ................................................................. v
LIST OF FIGURES ........................................................................ viii
LIST OF TABLES ........................................................................... viii
LIST OF ACRONYMS AND ABBREVIATIONS ................................. ix

1 INTRODUCTION ......................................................................... 1
   1.1 Objective ............................................................................ 1
   1.2 Background ......................................................................... 1
       1.2.1 Oil in the Water Column ................................................. 2
       1.2.2 Detection Technologies ................................................ 2
   1.3 Approach ........................................................................... 3
       1.3.1 Contracting Approach .................................................. 3
       1.3.2 Performance/Capability Requirements ......................... 3

2 DESIGN CONCEPT DESCRIPTIONS ........................................... 4
   2.1 Technology Overview ........................................................ 4
   2.2 NORBIT Wide Band Multibeam Acoustic Camera .................. 6
       2.2.1 System Description/Overview ........................................ 6
       2.2.2 Components ............................................................... 6
       2.2.3 Prototype Test Results ................................................ 7
       2.2.4 Further Development .................................................. 11
   2.3 WET Labs FINDS OIL .......................................................... 12
       2.3.1 System Description/Overview ........................................ 12
       2.3.2 Components ............................................................... 12
       2.3.3 Experiment Results ..................................................... 13
       2.3.4 Further Development .................................................. 15
   2.4 WET Labs WINDOW ............................................................ 17
       2.4.1 System Description/Overview ........................................ 17
       2.4.2 Components ............................................................... 18
       2.4.3 Experiment Results ..................................................... 18
       2.4.4 Further Development .................................................. 20
   2.5 Requirements Matrix ........................................................ 21

3 OVERALL ASSESSMENT OF PHASE II POTENTIAL ................... 22
   3.1 General ............................................................................ 22
   3.2 NORBIT WBMS ................................................................. 22
   3.3 WET Labs FINDS OIL .......................................................... 22
   3.4 WET Labs WINDOW ............................................................ 23
   3.5 Summary ........................................................................... 24

4 CONCLUSIONS AND RECOMMENDATIONS .............................. 25
   4.1 NORBIT Sonar .................................................................... 25
   4.2 WET Labs FINDS OIL .......................................................... 25
   4.3 WET Labs WINDOW ............................................................ 26
TABLE OF CONTENTS (Continued)

5 REFERENCES ................................................................................................................................. 27
   5.1 USCG Internal References: Vendor-Specific Design Reports .................................................. 27
   5.2 Additional References .............................................................................................................. 27
APPENDIX A. RESPONSE TO SUBMERGED OIL ........................................................................... A-1
APPENDIX B. ACOUSTIC DETECTION OF OIL IN WATER COLUMN .............................................. B-1
APPENDIX C. OPTICAL DETECTION OF OIL IN WATER COLUMN ................................................. C-1

LIST OF FIGURES

Figure 1. WBMS sonar ....................................................................................................................... 7
Figure 2. Computer model of AUV with WBMS mount ........................................................................ 7
Figure 3. Water in water test set-up ......................................................................................................... 8
Figure 4. Water in water test results ...................................................................................................... 8
Figure 5. Ohmsett pre-test set-up ........................................................................................................... 9
Figure 6. WBMS image with no plumes present ....................................................................................... 9
Figure 7. Sonar image of dispersed oil plume (tea leafs) entering the water column ............................... 10
Figure 8. Sonar image of a dispersed oil plume deeper in the water ............................................................ 10
Figure 9. Proposed test set-up for Phase II ............................................................................................ 11
Figure 10. Schematic of WETStar optical sensor ................................................................................ 12
Figure 11. Photos of baffle flasks with oil samples ................................................................................. 14
Figure 12. Bar chart showing F1 values for various oils + CDOM and blank samples .............................. 14
Figure 13. Relationship of FIR and density at two different DOR ............................................................ 15
Figure 14. Relationship of DOR and FIR ................................................................................................. 15
Figure 15. Schematic of towed body shown with transparent skin ............................................................ 16
Figure 16. WINDOW conceptual system design ...................................................................................... 18
Figure 17. Derived oil densities from inversion results ........................................................................... 19
Figure A-1. Heavy oil from a vessel submerged in water column ............................................................ A-2
Figure A-2. Schematic drawing of subsea blowouts for medium (left) and deep (right) wells ................ A-3
Figure B-1. Illustration of sonar interaction with multiple scatterers ....................................................... B-1
Figure C-1. Light scattered at angle $\theta$ by an object of refractive index $n$ and of size $d$ illuminated by an incident light wave of wavelength $\lambda$. Adapted from Marcos et al., 2011 ........................................... C-2

LIST OF TABLES

Table 1. Requirements matrix ............................................................................................................... 21
Table 2. Summary of system advantages and disadvantages ............................................................... 24
LIST OF ACRONYMS AND ABBREVIATIONS

AUV          Autonomous Underwater Vehicle
BAA          Broad Agency Announcement
CDO          Chemically dispersed oil
CDOM         Colored dissolved organic matter
COTS         Commercial-off-the-shelf
CRRC         Coastal Research and Response Center
CTD          Conductivity, temperature, and depth
CW           Continuous wave
DO           Dissolved oxygen
DOR          Dispersant to oil ratio
DSP          Digital Signal Processor
ECObbCD      Backscattering and fluorescence sensor
Ex/Em        Excitation and emission
FI           Fluorescence index or intensity
FINDS OIL    Fluorescent IN-situ Detection System for OIL
FIR          Fluorescence intensity ratio
FLS          Forward-looking sonar
FPGA         Field-programmable Gate Array
GPS          Global Positioning System
GUI          Graphical user interface
kHz          Kilohertz (1000 cycles/second)
LA           Louisiana
LED          Light-emitting diode
LISST        Laser In Situ Scattering and Transmissometry
LUT          Look-up table
M/T          Motor tanker
MASCOT       Multi-Angle SCattering Optical Tool
MC           Macondo
μm           Micron (10^{-6} meters)
nm           Nanometer (10^{-9} meters)
No.          Number
NOAA         National Oceanographic and Atmospheric Administration
NRC          National Research Council
Ohmsett      Oil and Hazardous Material Simulated Environmental Test Tank, now called The
              National Oil Spill Response Test Facility
OPA 90       Oil Pollution Act of 1990
OWR          Oil-to-water ratio
LIST OF ACRONYMS AND ABBREVIATIONS (Continued)

ppb  Parts per billion
ppm  Parts per million
R&D  Research and Development
RDC  USCG Research and Development Center
ROV  Remotely Operated Vehicle
SMART Special Monitoring of Applied Response Technologies
U.S. United States
USCG U.S. Coast Guard
UV   Ultraviolet
VSF  Volume scattering function
WAF  Water accommodated fraction
WALS Wide-angle-light scattering
WBMS Wide Band Multibeam Sonar
WET Labs Western Environmental Technology Laboratories Inc.
WINDOW Wide-angle-scattering Inversion to Detect Oil in Water
1 INTRODUCTION

The Deepwater Horizon oil spill in the Gulf of Mexico was a case that revealed several glaring technological gaps in responding to oil spill disasters. One of the issues was determining the size and location of subsurface plumes and making timely decisions to prevent significant ecological damages. While some advances were made during the Deepwater Horizon incident for tracking underwater plumes, a robust, quick, and efficient technology for scanning and sampling the water column to determine the extent of an oil plume and characterize the oil in the plume (oil type, concentration, droplet size, and physical properties) is needed. The technology would need to provide data in real-time and be presented in an easily comprehensible format to enable a more efficient monitoring of the submerged plume and possible initiation of countermeasures and recovery.

Most spills occur over a shorter period of time and closer to shore than the Deepwater Horizon oil spill. Often there is a very short timeframe for decision making to protect the environment and critical infrastructure by closing water-intakes, booming sensitive wildlife areas and important commercial facilities located along the shore and on rivers, and initiating dispersant application or oil recovery operations. Challenges in detecting oil within the water column include poor visibility, difficulty in tracking oil movements in fast-moving currents, and not being able to discover very low levels of oil or dispersed oil at all depths. Current subsurface oil sensing technologies are tailored for detecting oil at a single location and must be moved along numerous transects over a period of time to accurately map contamination horizontally and vertically. Often the configuration and location of an oil plume will have changed by the time the data from the surveys are processed and disseminated.

1.1 Objective

To address this technology gap, the USCG Research and Development Center (RDC) is undertaking a Research and Development (R&D) effort to identify and/or develop a system that can detect and characterize oil that is entrained and dispersed in the water column. This report summarizes the results of Phase I (Concept Design) of the effort in which remote sensing technology developers were solicited through a Broad Agency Announcement (BAA) to configure and describe systems that were at least at the proof-of-concept stage of development that could potentially address the remote sensing of oil in the water column. Two vendors responded describing and proposing three systems for further development in three separate reports. This effort is a part of a larger effort in the R&D program to develop countermeasures against oil spills. The next phase (Phase II – Development and Testing) involves further development, refinement and integration of the technology components in a field-deployable configuration, and testing prototypes in a simulated oil spill environment at the Ohmsett facility (Oil and Hazardous Material Simulated Environmental Test Tank, now called The National Oil Spill Response Test Facility).

1.2 Background

The Oil Pollution Act of 1990 (OPA 90) requires that Federal agencies conduct a coordinated research program, in cooperation with academic institutions and private industry, to improve the nation’s capability to detect, monitor, and conduct countermeasures, cleanup, and remediation operations to respond to accidental oil spills. Responding to oil spills on the surface of the water is often a difficult task with recovery rates generally averaging about 20 percent or less of the oil spilled. Responding to spills of
Detection of Oil in Water Column: Sensor Design

submerged oil is far more complex due to the problems associated with operating in an underwater environment where oil is spreading and dispersing in three-dimensions, visibility is limited, deploying divers is dangerous, and recovery equipment must be far more robust and complex than that used on the surface. However, a number of recent spills involving heavier oils that sink below the surface, as well as the subsurface oil encountered in the Deepwater Horizon spill, underscore the need for improving technology for subsurface oil spill response. A concise summary of the problems and technologies associated with submerged oil is provided in Appendix A and discussed in detail by Fingas (2011).

1.2.1 Oil in the Water Column

The term submerged oil generally refers to any oil that is not floating on the surface. In an oil spill involving submerged oil, three location scenarios are possible (these are further described in APPENDIX A):

- **Overwashed**: thicker oil that is floating near the water surface but is covered by a layer of water due to wave action. This can obscure the oil slick from visual monitoring and remote sensing at the surface.
- **Suspended**: oil globules or droplets are neutrally buoyant at depth and move in the water column under the influence of currents.
- **Sunken**: oil that is negatively buoyant and rests on the bottom of the water body. (Detection technologies for sunken oil were addressed in a previous USCG RDC study and reported in Hansen et. al, 2009).

Spilled oil can be suspended in the water column in a number of ways, which can be considered in roughly three distinct scenarios. The physical and chemical properties of oil resulting from these three scenarios can be very different and change with time. Submerged oil can come from a number of sources:

- Heavy oils from a surface spill that tend to sink under certain conditions, and is generally called submerged oil while it is in the water column and sunken oil when it reached the sea bottom.
- Oil rising to the surface from a subsea blowout.
- Fine droplets of oil resulting from chemical dispersants being applied to either a surface spill or subsea blowout or due to natural dispersion.

As described by the National Academy of Sciences (1999), Michel (2006), and Fingas (2011), each of the above scenarios presents its own challenges depending on the location and condition of the oil. This is particularly true when attempting to detect, identify, and characterize oil that is suspended in the water column. Physically capturing oil samples using rope and net snares towed through the water column has been employed in several spills, but is labor intensive and provides only a general indication of the amount of oil, geographical location and depth.

1.2.2 Detection Technologies

A brief summary of the capabilities and limitations of various detecting technologies is provided here. A more detailed discussion is provided in Appendices B (acoustic) and C (optic).

Utilizing sonar technology, which relies on the detection of an acoustic anomaly in the water column, is logistically easier and provides better areal coverage, which are characteristics of an ideal surveying tool. However, it is subject to false positives in that other sunken and suspended materials may provide an acoustic signature similar to that of oil. With current sonar systems, extensive data processing, verification
sampling, and/or subjective input from a highly trained analyst are required to positively identify the material as oil.

Optical detection and identification systems such as video cameras, towed fluorometers, and laser systems (e.g. laser line scan systems, laser fluorosensors, and laser induced scattering and transmission systems) all have their own limitations. Video systems are limited by the turbidity in the water column in locating and positively identifying oil. Towed fluorometers require the presence of aromatic hydrocarbons to trigger the fluorescent response, which are not necessarily present with heavier oils that are likely to become submerged. Although fluorometers are capable of detecting, identifying, and characterizing the oil in a captured sample, sampling is discrete at a certain point and the results are not necessarily applicable to other locations in the water column. Mapping of the oil plume therefore requires multiple samples at various depths over a wide area which is time consuming, and may be invalidated altogether if the plume is moving and changing configuration.

Laser systems are generally limited in the depth of water that can be penetrated by the laser and are often susceptible to false positives from naturally occurring marine materials. They are also generally more complex, expensive, and require greater power input than the acoustic or fluorometric systems.

Accordingly, it is not a foregone conclusion that any system proposed in response to the BAA will be entirely successful in detecting, identifying, and characterizing suspended oil in all configurations and all locations. The specifications in the BAA thus represent a performance target for researchers developing and testing remote sensing systems for suspended oil.

1.3 Approach

1.3.1 Contracting Approach

The RDC developed specifications and released a BAA in November 2011 calling for a two-phased approach to detection of oil within the water column. The scope of the BAA included Phase I (Design Concept) and an option for Phase II (Prototype Development and Testing). The RDC received eight responses (seven vendors) to the BAA. It chose three ideas for Phase I proof-of-concept description and preliminary testing. These included:

- NORBIT Wide Band Multibeam Sonar (WBMS)
- Western Environmental Technology Laboratories Inc. (WET Labs) Fluorescent IN-situ Detection System for OIL (FINDS OIL)
- WET Labs Wide-angle-scattering Inversion to Detect Oil in Water (WINDOW)

1.3.2 Performance/Capability Requirements

The BAA specifications required the contractor to develop a design concept for a prototype oil detection system. The BAA specified that this system be able to detect, identify and characterize commonly spilled light oils (diesel), crude and heavy oils, such as Bunker C oil, that may be temporarily suspended in the water column. The system must also have the ability to quickly process and plot the data and relay the information in an easily interpreted format to allow spill responders to make timely key decisions regarding mitigation and countermeasures.
Detection of Oil in Water Column: Sensor Design

The BAA further specified that the design concept demonstrate as many of the following capabilities as possible (they are ranked in importance):

1. Provides results in near real time (less than 1 hour);
2. Calibrates easily for different oils;
3. Detects oil at depths up to 200 feet;
4. Works in currents or tow speeds up to 5 knots;
5. Reports minimal false alarms;
6. Allows smooth data flow from field to command center;
7. Detects dispersed crude oil at levels of 0.5 parts per billion (ppb) or lower;
8. Sweeps an area of water column 3 feet by 3 feet;
9. Provides digital readout or measured values and digitally logs field data;
10. Is field rugged;
11. Is portable;
12. Compatible with fresh and salt water;
13. Determines droplet size, density (specific gravity) and/or kinematic viscosity;
14. Adapts to various depths (deep vs. shallow);
15. Operates from vessel in variety of conditions;
16. Deploys quickly and easily;
17. Measures dissolved oxygen (DO); and
18. Grabs water samples for further laboratory testing.

2 DESIGN CONCEPT DESCRIPTIONS

2.1 Technology Overview

The design concepts presented here represent three distinct detection technologies:

- Acoustics (sonar) (i.e., NORBIT WBMS).
- Ultraviolet light fluorescence (i.e., WET Labs – FINDS OIL).
- Scattering of light (i.e., WET Labs – WINDOW).

The first two methods have already been used for oil detection in the marine environment. Acoustic methods rely on the differential acoustic properties of oil compared to those of water because of the different densities and sound speeds of the materials. The acoustic data are generally geo-referenced using Global Positioning System (GPS) data and mapping software. According to Schnitz and Wolf (2001), advantages of acoustic methods include potential utility when water depth or low visibility preclude visual observations, use at night, and the ability to search relatively large areas. Disadvantages include cost, limited availability of equipment and operators, slow deployment times in many areas, and potential for false positives in areas where the acoustic signature of other submerged material is similar to that of oil. Acoustic techniques generate enormous amounts of data that generally take several hours or days to process and verify. Expert data interpreters may be needed to interpret acoustic imagery and identify the targeted object or water property. Interpreted results must often be confirmed using direct sampling or other means (ground truth measurements).

A multi-beam sonar system (the RECON SeaBat system) operating in the frequency range of 200 Hz to 400 Hz was able to detect and map test oil samples on the bottom of the Ohmsett tank with a positive
identification accuracy of 80 percent (Hansen et al., 2009). Image interpretation was facilitated by knowing the configuration and type of oil presented to the sensor. Multi-beam sonar systems operating in the same frequency range have been used to detect suspended oil in the water column (Wendelboe, 2009). Although the tests were complicated by weeds and other debris at the pycnocline where entrained oil may concentrate, algorithms were developed to interpret the acoustic backscatter signals to detect oil with a 90 percent success rate. Accordingly, sonar systems hold some promise for submerged oil detection and positive identification, particularly if the false positives from other materials can be resolved.

Fluorometry has become a standard technology in detecting the presence and concentration of hydrocarbons in the water column. In-situ and towed fluorometric detection systems are widely available and routinely used to detect and map petroleum leaks and spills (Turner Designs, 1999). Fluorometry can also be used to assess the effectiveness of dispersant application during a spill under the National Oceanographic and Atmospheric Administration (NOAA) Special Monitoring of Applied Response Technologies (SMART) protocols (at the Tier II or III levels). Fluorometric systems had not been routinely used for actual spills in the United States up until the Deepwater Horizon response but are used in Canada and the United Kingdom to assess the potential for tainting fish from subsurface oils.

Fluorometry can also be used to detect hydrocarbon presence which may warrant the shutdown of water intakes. This method was used at the motor tanker (M/T) Athos 1 spill to monitor for oil entering water intakes at a facility and along transects in the Delaware River. However, all readings were at background, even when there was visible oil on the water surface. Fluorometry was employed in attempting to monitor dispersed/submerged oil and gas from the DeepSpill simulated oil blowout test off Norway (Johansen et al., 2003). Fluorometric techniques were also used to determine oil concentration in the water column during the Deepwater Horizon spill in 2010.

Fluorometry relies on the presence of aromatics and may not be an appropriate method for heavy oils that have low dissolved fractions of oil and form larger oil droplets that pose difficult calibration problems. Fluorometry is also limited to sampling oil in a relatively discrete segment of the water column, and multiple samples at various depths along several transects must be taken to map an oil plume. Although restricted to making oil concentration measurements at discrete points in the water column (Brown et al., 1997), fluorometers have a detection range from parts per billion to parts per million, depending on environmental conditions and oil type.

Fluorometric systems may be mounted on buoys, boats, or remotely operated vehicles. When mounted on boats and coordinated with GPS, they can provide maps of the subsurface oil concentration field. Given the three-dimensional nature of submerged oil plumes, mapping of subsurface oil requires an extensive effort. Towed systems might also be used to monitor conditions at one location, such as in a river or coastal inlet, to determine whether oil has reached that location and is being transported downstream.

Optical backscattering is used to determine the level of suspended material in the water column. Backscattering measurements rely on the principal that the reflective and refractive index of light returned from spherical particles in the water column can be correlated with the concentration and size distribution of the particles. Optical backscattering sensors are commercially available for determining the amount of suspended material in the water column (turbidity), and could be used to detect and characterize dispersed oil droplets. The important unresolved issue is whether the data can be processed and analyzed to conclusively identify the suspended material as hydrocarbons vs. other suspended materials.
The following sections describe the results of the three Phase I (Design Concept) efforts as reported by the companies engaged in the development efforts awarded under the BAA. No effort is made in this report to critically analyze or corroborate the findings of the three reports. An overall assessment of the status and potential of the three technologies being proposed is provided, discussing the inherent advantages, disadvantages, and potential for Phase II testing at Ohmsett.

### 2.2 NORBIT Wide Band Multibeam Acoustic Camera

NORBIT’s Wide Band Multibeam Sonar (WBMS) platform was developed over the last 3 years. It is based on modern components and extensively uses Field-Programmable Gate Array (FPGA) as well as Digital Signal Processor (DSP) technology to maximize the flexibility of the system. This creates a very flexible platform as most aspects of the sonar can be changed in firmware and does not require extensive redesign.

#### 2.2.1 System Description/Overview

NORBIT utilizes the WBMS as an acoustic sensor to provide 3D topology of the oil plume. The WBMS sonar (Figure 1) is specifically designed as an ultra wide band (160 kilohertz (kHz) band width) very compact unit, with low power consumption. It operates at a nominal frequency of 400 kHz. Also, the sonar has integrated processing capabilities so that processing of water column scatters can be generated in the sonar head itself. The system has been fully configured and is readily deployable on a towed vehicle, remotely operated vehicle (ROV), or Autonomous Underwater Vehicle (AUV).

#### 2.2.2 Components

The WBMS platform has a very simple design, with the sonar transducers and processing integrated in a single unit. This makes it easy to adapt the sonar to various platforms, as some signal processing can be done in the sonar itself, although access to time series data storage is required. Access to time series data can be facilitated either by storage of the data locally in the system or in the platform carrying the sonar or, if possible, topside on a computer.

Potential platforms include:

- Bottom mounted observatory.
- Ship mount.
- Towed platform.
- Unmanned drone.
- Glider mounted.
- Autonomous Underwater Vehicle (AUV) (Figure 2).
- Remotely Operated Vehicle (ROV).
2.2.3 Prototype Test Results

Some tests have been conducted prior to the Phase II testing. This was done primarily to reduce the risk on non-performance for the tests in Phase II and improve on the set up scenarios for Phase II testing. The test demonstrated the sonar's capabilities to differentiate between two fluids with relatively small impedance differences. The test involved the release of a fresh water plume at dockside in a salt water environment. The fresh water was allowed to rise to the surface naturally due to its lower density relative to salt water. In this test the temperatures were almost identical, so the salinity caused the density difference between the two fluids. This gives a very small impedance difference when the sound waves enter the plume area. The test setup is depicted in Figure 3. The fresh water in salt water test produced a discernible acoustic anomaly in the scan as noted in the circled anomaly in Figure 4.
Figure 3. Water in water test set-up.

Figure 4. Water in water test results.
Another pre-test, this time using dispersed oil in water (oil treated with dispersant) was conducted at Ohmsett in August 2012. The test was done in conjunction with the trials being conducted by an oil company, where the objective was to test dispersant effectiveness on various hard-to-disperse oil types. The best dispersed oil plume was produced during the first tests on Tuesday as well as Friday afternoon of the test period; on other days limited oil plumes were produced (Eriksen, et al., 2012).

Two sonars were used in the set-up. Sonar configurations were both in the normal forward-looking sonar (FLS) mode and in a vertical mode “scanning” the tank. Both sonars were mounted at mid-water in the column oriented horizontally across the longitudinal axis of the tank throughout the experiment. The test set-up is shown in Figure 5.

An image with no plumes present is shown in Figure 6. Figure 7 shows an acoustic anomaly associated with the dispersed oil plume entering the water column. Figure 8 shows a plume deeper in the water. The dense green lines represent the water surface and the bottom of the tank.
Detection of Oil in Water Column: Sensor Design

Figure 7. Sonar image of dispersed oil plume (tea leafs) entering the water column.

Figure 8. Sonar image of a dispersed oil plume deeper in the water.
2.2.4 Further Development

The system is generally mature enough to be used for the Phase II test. There are several areas where improvements may be sought if a follow on contract is awarded: a.) acoustics, b.) firmware, and c.) software and data processing.

2.2.4.1 Proposed Ohmsett Test Plan

Figure 9 provides a sketch of the suggested test-setup for Phase II testing at the Ohmsett facility. The second sonar might not be needed for this test. The sonar mounted on the pan tilt device might be equipped with a narrow angle projector subsystem, which can be configured to illuminate various opening angles. Sonar(s) needs to be connected to a computer on the bridge, along with the pole used for the mounting of the sonar and pan tilt device.

![Proposed test set-up for Phase II.](image)

2.2.4.2 Limitations

The physical size of the Ohmsett test tank limits the ranges where detection of oil is possible in the tank. Also, the reflections from the tank walls may interfere with the detection of oil. However, it is possible to establish a detection threshold from shorter range data not subject to the interference from the tank reflections, which can be scaled to longer ranges to assess detection effectiveness.

An open water test would be most optimal for this test, as the tank walls will provide some limitations, since the tank acts as a hard reflector. But as it has been shown during the August 2012 test at Ohmsett, the test can be performed successfully at this test facility, and Ohmsett provides the best simulated oil spill environment for testing. With the proposed test setup, the two sonars are facing horizontally and vertically, but looking upwards to avoid directly facing towards the tank bottom or walls.
2.3 WET Labs FINDS OIL

2.3.1 System Description/Overview

The Fluorescent IN-situ Detection System for OIL (FINDS OIL) system is comprised of a towed body containing multiple sensors, software, and a data transfer system. Sensors for multi-parameter sensing provide hydrographic properties, oil detection, oil property estimation, and are used to minimize false positives. The mixing integration sensor will measure fluorescence and backscatter and be mounted at the rear of the towed body to sample the mixed volume of water entrained behind the towed body. The other sensors (Multichannel WETStar; dissolved oxygen sensor; and conductivity, temperature, and depth (CTD) sensor) are flow-through sensors such that water is pumped through the sensor from an intake at the center of the nose cone to an exit port on the side of the towed body. The towed body was designed to meet the system capabilities (200-foot depth, 5 knots, rugged, etc.). Response software, field telemetry, and online database were designed to facilitate ease of operation, real-time mapping, and reliably quick transfer of data to the command center.

The WETStar fluorometer allows the user to measure relative chlorophyll, colored dissolved organic matter (CDOM), or other concentrations of fluorescing materials (e.g. hydrocarbon aromatics) by directly measuring the amount of fluorescence emission from a given sample of water illuminated by an ultraviolet (UV) light source. The sample media is pumped through a quartz tube mounted through the long axis of the instrument. These samples, when excited by the WETStar internal light source, absorb energy in certain regions of the visible spectrum and emit a portion of this energy as fluorescence at longer wavelengths.

The WETStar utilizes three excitation and emission (Ex/Em) pairs for CDOM discrimination, fluorescence intensity ratio (FIR) calculation, and oil concentration. The FIR is used as an index to explain how well oil is dispersed in a given water body (Kepkay, et al., 2011).

2.3.2 Components

The FINDS OIL system contains the following components:

1. Multichannel WETStar Sensor (Figure 10).
   a. Sensitive oil detection, discrimination from background (elimination of false positives), and property estimation (density, dispersion efficacy).

![Figure 10. Schematic of WETStar optical sensor.](image-url)
Detection of Oil in Water Column: Sensor Design

2. CTD Sensor.
   a. Depth feedback for towing and mapping, salinity and temperature hydrographic parameters. Temperature data are required for accurate oil concentration determination.

3. DO (Dissolved Oxygen) Sensor.

4. Integration sensor (ECObbCD: backscattering and fluorescence).
   a. A means for the towed body to analyze a sample representative of a much larger volume than permissible with point source fluorometers in the WETStar sensor. Fluorescence and scattering are used to reduce false positives and ensure that oil identification and characterization provided by WETStar sensor is typical of hydrocarbons in the surrounding water column. Provides sensor with the potential for upgrade to oil specific scattering sensing technology.

5. Data logger.
   b. Data logger has multiple ports to distribute power and log sensor data. Data logger collates sensor data and timestamps.

   a. Multifunctional towing cable providing power distribution, and near real-time data transfer.

7. Towed body platform.
   a. Nose cone with bolt-on accessories.
   b. Instrument core for housing sensors and stabilizing towed body.
   c. Tail fin stabilizer section.

8. Control computer: ruggedized tablet.

9. Response software (data readout, mapping, and hierarchical analysis).

10. Telemetry, GPS, and database (data to command center).

11. Power source: deep cycle battery.

2.3.3 Experiment Results

Various oil types from refined, fuel, and light-heavy crude oils, with and without dispersant and background organic matter, were analyzed with the system. Tests demonstrated the ability of the system to detect low levels of oil, determine dispersant to oil ratio, determine oil type based on density relationships, and discriminate oil from background CDOM. Oil types introduced to the WETStar sensor are shown in Figure 11. These include:

A. SynCrude (from Athabascan Tar Sands) chemically dispersed oil (CDO) (oil-water ratio (OWR)=1:1200, dispersant to oil ratio (DOR) =1:25).
B. Louisiana (LA)-Sweet CDO (OWR=1:1200, DOR=1:50).
C. Macondo (MC)-252 CDO (OWR=1:1200, DOR=1:50).
D. MC-252 water accommodated fraction (WAF).

Figure 12 shows fluorescence index (FI) values for various oils + CDOM and blank samples. FI values are beneficial in that they distinguish between physically and physically/chemically dispersed oil in a water body (Kepkay, et al., 2011). The higher the FI value, the less likely the oil is chemically dispersed. Note that CDOM levels chosen range from typical estuarine levels to levels for extremely high CDOM rich rivers.
Figure 11. Photos of baffle flasks with oil samples.

Figure 12. Bar chart showing FI values for various oils + CDOM and blank samples.

Figure 13 shows the variation in FIR as a function of density for two different DORs. Relationships demonstrate positive correlations, with FIR regions that are distinctive to certain oil densities. Oil density variation over a temperature range of 0-35°C is less than one percent. Figure 14 shows the effect of DOR on FIR for both heavy and light crude oils. For the heavy oil, a highly correlated relationship is developed; while for the light oil, a lower correlation still permits grouping DORs. The FIR is not shown for WAFs as it is several factors higher than dispersed oil FIRs. Evaluation of sensor response to just dissolved oil components in the WAF demonstrates the ability to detect oil in spills without dispersant added or where fine particles haven’t formed. Additionally, these results demonstrate that fluorescence can be used to estimate the level of dispersant added to a spill.
Detection of Oil in Water Column: Sensor Design

2.3.4 Further Development

Specific developmental activities needed to complete the final design, if a follow on contract is awarded include:

- Component Acquisition: purchase of materials and components not in-house.
- Multichannel fluorometer refinement: application of Phase I findings to multichannel fluorometer design. Higher power light source integration, source driver circuitry for more stable light source performance, flow tube design for better optical coupling, detector circuitry for on-scale performance at higher oil concentrations (>3000 parts per million (ppm)). System calibration and temperature response confirmation.
- Graphical user interface (GUI) development: includes the software development tasks associated with creation of the Response GUI, coding the algorithms for hierarchical analysis and oil concentration determination, and control of the telemetry system.
2.3.4.1 Tow Testing
Towed body build: includes construction of the towed body frame and skin for the three sections, construction of the depressor plate, the instrument mounting tray, assembling of sections, and mounting of the instruments. It includes development of the flow path for flow-through sensors and mounting of the mixing integration sensor. Figure 15 shows a schematic of the towed body with transparent skin to show instrument shape and positioning (data logger is blue). Depressor plate is shown for deep towing.

Figure 15. Schematic of towed body shown with transparent skin.

Database development: includes creation of a singular database for collection of both data sent from the cellular modem and the iridium satellite modem. The database will then be password protected and designed to send notifications via email and data (jpeg of mapped oil concentration and properties). The database will be structured to organize data, provide metadata, and provide versioning control.

System component integration and testing: includes connection of sensors to the data logger, minor modification for data logger firmware to integrate the data logger with the software, hardware adaptation for RS-422, integration of the electromechanical tow cable with the data logger and system computer, and integration of the software GUI with the system computer.

Telemetry development and testing: includes housing the Iridium antenna and precision GPS antenna in a combined housing and integrating telemetry with the software. Telemetry testing will include testing transfer of data to the command center from various remote locations (through obstacles such as buildings and trees and over long distances) and testing of database functionality for notification and push of data to command center.

Tow testing is planned for approximately 3 day-long tow tests off the Oregon coast. Tow testing is designed to optimize platform weight, buoyancy, depressor plate angles, and deployment protocols. Test results will generate approximate relationships between tow speed, cable length, and depth to ensure ease of use. Offshore testing will also ensure full system integration, communication, and telemetry efficacy from remote sites. Vessels utilized for the test will be small boats (e.g., small crabbing skiffs and/or small fishing vessels) capable of towing up to 5 knots to simulate usage on vessels with limited space and accessories (such as Zodiacs).
Detection of Oil in Water Column: Sensor Design

2.3.4.2 Prototype Demonstration at Ohmsett

After tow testing, a report will detail recommendations for testing of the system at Ohmsett and any limitations to testing of the desired capabilities. Approximately 4 days of testing of system capabilities is planned.

2.3.4.3 Limitations

The system is based on optical methods, and while robust, there are typical optical limitations. If the system is towed through a significant volume of liquid oil not dispersed in water, optics may foul and require retrieval and simple cleaning. Fouled sensors will saturate and will still be effective at mapping the plume, but will not be sensitive to smaller oil concentrations nor have the low detection limits needed to map plume edges. Optical measurements are also susceptible to natural water clarity.

Specific tests or limitations on equipment (e.g. special power requirements, minimum depth of water, space needed, etc.)

- 1-2 operators needed (P.I. and field tech for demonstration)
- Minimum depth: ~8.5’ (can be towed at the surface)
- Maximum depth: >200’ (Cable length ~650’ for ~212’ depth; sensors 600 m (12,700’)).
- Minimum system space: 38” x 14” x 8.5” submersible space for towed body testing (as if in tank) and 18” x 18” x 18” inch space to accommodate battery, telemetry, and tablet computer on deck.
- Operational time: 80 hrs until deep cycle battery recharge, 8 hrs until Yuma rugged tablet computer recharge (on-board extra hot swappable battery packs and charger facilitate continuous use).
- Operational temperatures: natural water temperatures (~liquid water; <0°C-100°C)
- Tow speed: 0 to >5 knots (can use weights to perform stationary depth profile). Note that the system will require distance to slow down and stop after towing.
- Detection limit: ~36 ppb. Able to detect Water Accommodated Fraction (non-chemically or physically dispersed oil, able to detect dissolved hydrocarbons).

2.4 WET Labs WINDOW

2.4.1 System Description/Overview

The WET Labs WINDOW design is a compact, multi-angle scattering instrument with an automated inversion algorithm and intuitive smart phone display that will quantify the size distribution and abundance of emulsified oil droplets in water and determine the refractive index of the oil to readily derive density and viscosity.

The technique of wide angle scattering relies on the dependency of light refraction and reflection on the sizes and refractive indexes of the particles. For oil emulsions, the latter (refractive index) is a close analog to density and viscosity (Vargas & Chapman, 2010). Particles that are most readily detected and quantified with this technique are those that are nearly spherical, namely bubbles and oil droplets, because such particles produce spherical lensing effects characterized by distinct and unique constructive and deconstructive interference patterns in angular scattering. When superimposed on smooth, regularly shaped scattering functions from naturally occurring background particle populations, these unique scattering functions can be readily discriminated and then used to derive concentration, size, and density of the suspended emulsion.
2.4.2 Components

The entire sensing system will consist of an in-water sensing package, surface deck unit with laptop computer and integrated GPS, and a deep cycle 12 VDC battery if ship power is not available. Data in the form of mapped oil properties will be broadcast wirelessly through the cellular network from the laptop computer and will thus be made available to all interested parties with cellular access.

The sensor system will be deployable by hand or from a compact, portable hoist system or a maneuverable, variable-depth towed package, allowing profiling from small boats. Limitations for towing speeds will generally be dependent on the towed vehicle and vessel, but towing speeds up to 10 knots have been demonstrated previously with similar sensors. A single operator will be able to deploy the entire system.

Figure 16 shows the conceptual system design, depicting transfer of raw data from the Environmental Characterization Optics (ECO) sensor to a surface deck unit with operator GUI and data display on a laptop PC, to wireless broadcasting of compressed, low file size jpeg pictures of relevant data for any parties involved in an oil spill response via easily accessible smart phone technology. Larger files in kml format compatible with Google Earth will also be broadcast that will contain several additional layers of information that will plot automatically for computers equipped with free Google Earth software.

![Figure 16. WINDOW conceptual system design.](image)

2.4.3 Experiment Results

Through Phase I testing, the method and inversion algorithm have proved capable of quantifying emulsion size distributions and density with very good accuracy (within several percent), verified with ancillary measurements from holographic imaging. Phase I testing included the natural condition of emulsions suspended among a complex mixture of naturally amorphous aquatic particles with broad size range.

The primary objective of Phase I lab testing was to quantify the accuracy and sensitivity of the technique for emulsions of different oils in natural seawater. Three sets of experiments were first carried out with emulsions suspended in purified salt water, so that the emulsions themselves were the primary scattering component of the hydrosols. Oils of low, medium, and high refractive index were separately emulsified in
solution for each experiment. Following these experiments, another set was carried out using the same emulsified oils, but with a background of purified salt water containing a broad size distribution of suspended sediments collected from Narragansett Bay. This set of experiments provided a direct analog to oil emulsions suspended in natural seawater with a complex mixture of background particles. For all experiments, after the background media was prepared in a testing tank, emulsified oil was added from a stock solution sequentially to create a suspension series, with measurements made at each concentration. Inversion algorithms in various forms of refinement were then applied to the data to derive the concentration, size distribution, and refractive index of the emulsified oil. Accuracies in size distributions and concentrations were evaluated from coincident measurements with a digital holographic imaging microscope. The refractive index of each oil solution was considered known previously from literature.

Figure 17 shows derived oil densities from inversion results. The emulsion oil density was estimated as the average of the densities of each subpopulation weighted by their respective concentration. The solid points at Measurement No. (number) zero (0) and the associated dashed lines are the presumed densities of the oils from the literature. Derived oil densities are in satisfactory agreement with literature values.

![Figure 17. Derived oil densities from inversion results.](image)

WET Labs summarized the test results as follows:

- The theoretically expected mid-angle enhancement from emulsified oil droplets has been verified experimentally.
- The inversion technique is effective in identifying the presence of oil droplets and quantifying their concentration with accuracy better than 10 percent.
- The inversion technique is effective in quantifying size distributions of emulsified oil droplets with precision of 1-2 microns (μm) in determining modal droplet size.
- Size distributions of emulsified oil droplets were completely dominated by droplets <20 μm, with modal peaks ranging from about 3-6 μm.
Detection of Oil in Water Column: Sensor Design

- The inversion technique is effective in quantifying emulsified oil density with accuracy generally better than two percent. Because a high degree of aggregation of particles did not occur during this experiment, scattering functions representing aggregate subfractions were not used in the inversion library. If used, one can expect an increase in accuracy in quantifying oil density when aggregation does occur although this is a challenge in itself. Truncating the angular range of scattering used in the inversions to 70 to 150 degrees produced similar results as using the full angular range of 10 to 170 degrees, indicating that the ECO sensor line can be effectively employed to quantify oil concentration and density with this technique.
- Optical windows can be rapidly fouled by dispersed oil, requiring wiping of the interface to ensure accurate results.

2.4.4 Further Development

2.4.4.1 Prototype Development and Testing

The inversion algorithm computing emulsion size distribution, density, and viscosity currently executes in about 25 seconds for 30 second intervals of 1 Hz data. If a follow-on contract is awarded, WET Labs plans to transition the algorithm libraries into simple look-up tables (LUTs) that will be able to provide derived oil emulsion parameters from measurements of scattering in real-time during collection.

The sensor suite for the oil detection system will consist of:

ECO- VSF sensors, each measuring scattering at 3 angles (9 total scattering measurements with angular resolution of 70 to 150 degrees in 10 degree increments); each sensor head will have an automated rotating wiper to keep the optical windows clean.

- SeaBird Electronics SBE49 conductivity, depth, and temperature sensor.
- SeaBird Electronics SBE63 optical dissolved oxygen sensor.

WET Labs will recommend how best to test the WINDOW system to demonstrate that the prototype meets the operational conditions specified. These recommendations will be incorporated into the Government’s test plan. The Ohmsett facility in Leonardo, NJ, is the anticipated initial test location. Testing will occur in the large tow tank or equivalent. The time period for testing is anticipated to be in November 2013. WET Labs will ship the equipment to the test facility and demonstrate the WINDOW system’s capabilities. A maximum of four days is anticipated to fully demonstrate prototype capabilities.

2.4.4.2 Limitations

According to WET Labs, the biggest potential limitation is the challenge of accurately representing in the inversion library the scattering characteristics of emulsified oil aggregated with other oceanic particles. Through Phase I testing with high concentrations of background suspended sediments, aggregates were found in some cases to be another particle type or sub-fraction requiring its own specific scattering functions in order for the inversion to be as accurate as possible. Aggregations can form complex scattering patterns that can be challenging to model. Since this has not previously dealt with the explicit problem of aggregation in the inversion models, this can be considered an area of risk in their Phase II work, where it will be addressed.
2.5 Requirements Matrix

Table 1 summarizes how each system meets the BAA requirements, listed in order of importance.

Table 1. Requirements matrix.

<table>
<thead>
<tr>
<th>Capability</th>
<th>NORBIT WBMS</th>
<th>WET Labs FINDS OIL</th>
<th>WET Labs WINDOWS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Provides results in near real time (less than 1 hour)</td>
<td>Depends on platform</td>
<td>Constant</td>
<td>Demonstration results provided in &lt; 1 minute</td>
</tr>
<tr>
<td>2. Calibrates easily for different oils</td>
<td>Data processing is necessary</td>
<td>Factory calibrated</td>
<td>Factory calibrated</td>
</tr>
<tr>
<td>3. Detects oil at depths up to 200 feet</td>
<td>Depends on platform</td>
<td>Yes</td>
<td>Specified sensor package has a rating of 800 feet</td>
</tr>
<tr>
<td>4. Works in currents or tow speeds up to 5 knots</td>
<td>Yes</td>
<td>Yes</td>
<td>Function of deployment method</td>
</tr>
<tr>
<td>5. Reports minimal false alarms</td>
<td>Work needed</td>
<td>Multi-parameter data used to minimize false positives.</td>
<td>Reports of false positives or false negatives are not expected.</td>
</tr>
<tr>
<td>6. Allows smooth data flow from field to command center</td>
<td>Yes (wireless phone modem)</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>7. Detects dispersed oil at levels of 0.5 ppb or lower</td>
<td>More work needed to understand what is being detected; ppb not addressed.</td>
<td>Current system detection limits are 36 ppb.</td>
<td>Current detection limit for the scattering signal is about 10 ppb.</td>
</tr>
<tr>
<td>8. Sweeps an area of water column 3 feet by 3 feet</td>
<td>Yes</td>
<td>No</td>
<td>This is a point source measurement.</td>
</tr>
<tr>
<td>9. Provides digital readout or measured values and digitally logs field data</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>10. Is field rugged</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>11. Is portable</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>12. Compatible with fresh and salt water</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>13. Determine droplet size, density (specific gravity) and/or kinematic viscosity</td>
<td>Further tests are needed; probably not.</td>
<td>Oil density, dispersant-to-oil ratio, and an estimation of oil type will be provided.</td>
<td>Yes</td>
</tr>
<tr>
<td>14. Adapts to various depths (deep vs. shallow)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>15. Operates from vessel in variety of conditions</td>
<td>Yes</td>
<td>Yes</td>
<td>There are no foreseen limitations in terms of environmental conditions from a vessel</td>
</tr>
<tr>
<td>16. Deploys quickly and easily</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>17. Measures dissolved oxygen</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>18. Grabs water samples for further laboratory testing</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>
3 OVERALL ASSESSMENT OF PHASE II POTENTIAL

3.1 General

Having summarized the capabilities of the three systems addressed in Section 2, it is necessary to address the potential of these systems for further development and testing in Phase II. Again this assessment does not seek to verify the results reported by the vendors, but rather highlight the advantages and disadvantages identified by the vendors, as well as highlight general limitations inherent in the technology as reported in Appendices B and C.

3.2 NORBIT WBMS

The NORBIT WBMS system uses a well-developed, commercially available technology that has been used in various marine applications. The system proposed has already been configured and packaged in a compact, lightweight unit that is readily deployable for in-situ subsurface remote sensing on a towed body, ROV, or AUV. Because the system scans the water column with multiple beams of different frequencies, the detection of a range of acoustic anomalies is possible. The system can survey a wide area of the water column easily meeting the 3 feet by 3 feet areal coverage target cited in the BAA. The system has already been deployed and tested in the Ohmsett tank, albeit only for a short time.

The primary disadvantage of the system is the inability to conclusively discriminate petroleum hydrocarbons from other materials which may have a similar acoustic signature. Identification of the acoustic anomaly/material encountered often requires a complimentary sensing technology. The system may be able to detect oil in the water column, but positive identification and characterization may be difficult, especially if the oil disperses as individual droplets. There is no certainty that acoustic imagery will be able to determine oil concentration or physical properties. In addition, acoustic profiling at multiple frequencies generates a large amount of data which must be stored and processed. This may limit real-time availability of data and imagery to support rapid decision-making. Finally, computer-automated interpretation and mapping of acoustic imagery is challenging, and real-time interpretation currently requires subjective analysis by a trained operator.

It will be a challenge to assess the effectiveness of the sonar, particularly in terms of providing real time data, since this is dependent on the platform used. Further testing in the Ohmsett tank should focus on the system’s ability to readily detect the acoustic anomalies associated with continuous, relatively homogeneous oil plumes such as those generated by subsea releases or dispersant application to surface slicks. Tests should include several oil types at different concentrations (having different densities and acoustic impedances). It should also be tested for discrete streams and globules of oil entrained in the water column.

3.3 WET Labs FINDS OIL

The FINDS OIL system uses optical fluorometry and backscatter technologies implemented in a single towed body. Fluorometry has routinely been used to detect and characterize the aromatic fractions of petroleum hydrocarbons in water. Optical backscattering is routinely used to determine suspended particle concentrations in the marine environment. The two sensors integrated in a single probe provide a credible capability to map hydrocarbon concentrations in the water column. Laboratory calibration of both sensors is required to establish the oil identification library, but the calibration procedure is straightforward. Data processing, transmission (via towing cable), and presentation (via concentration contours in 3-dimensions) have been previously demonstrated with other towed fluorometers.
The primary limitation of previously used towed fluorometers is that they sample the water column at a specific point and do not provide information on the areal extent of the hydrocarbon contamination measured (such as the 3 feet by 3 feet areal sample window specified in the BAA). However, a suggestion is made that the inability to meet the 3 feet by 3 feet sample window can be remedied by a high data rate of 1 Hz and a spatial resolution of 0.51 meter per knot of tow speed. Additionally, the FINDS OIL system seeks to correlate measurements in the flow-through fluorometer with fluorescent backscatter measurements from a sensor mounted in the rear of the towed body facing backwards (aft). The concept is that water in front of the towed body will be entrained and homogeneously mixed in its wake such that if the fluorescent backscatter from the entrained water indicates the presence of oil even with the mixed volume 2 to 4 feet away from the instrument, then it can be assumed that the instrument is in an oil plume. However, the sensor on the rear of tow-body requires turbulence to gain proper mix of oil and water.

As with other optical sensors, fouling of the sensor window in heavy oil concentrations may be a problem and require periodic cleaning, particularly in the flow-through WETStar fluorometer. Fouling should not be a problem with the backscatter sensor facing aft.

This is a practical approach, with a large use of commercial-off-the-shelf (COTS) items. Further testing of the flow-through fluorometer is best handled in a laboratory setting, verifying the accuracy of the sensor with various oil types and concentrations. The capabilities of the backscatter fluorescence sensor to detect oil in a homogeneous oil-in-water dispersion can also be pursued in the lab. The system can then be configured for testing in the Ohmsett tank, with tank testing focused on the ability of the system to correlate oil identification and characterization in the WETStar flow-through fluorometer with the more pervasive oil presence in the volume sampled by the fluorescence backscatter sensor to accurately map the extent and oil concentration in the plume. This will require generation of a stable and homogeneous oil plume, which may itself be challenging.

3.4 WET Labs WINDOW

The Windows system is an adaptive application of a commercially available optical backscattering instrument (ECO-VSF) routinely utilized to measure suspended material concentrations (turbidity) in the water column. The adaptation is a development of inversion algorithms that allow determination of the oil droplet size and concentration of the suspended oil particles. Assuming constant physical properties for a specific type of oil (no weathering), density and viscosity can also be inferred. The system is lightweight, compact and readily deployable by a single individual. Although processing via the inversion algorithms currently introduces a time delay (less than 1 minute) in output availability, this can be overcome by development of LUTs which will allow real-time output and display. Data transmission and display is provided using current cell phone technology. Thus the hardware and software configuration for the system appears relatively straightforward.

The major challenge associated with the technology appears to be the workload in developing the inversion algorithms implemented in the LUT that account for the wide variety of oil types that might be encountered against varying backgrounds of other types of suspended material in a marine environment. The situation is further complicated by the existence of oil droplet-particulate material aggregates which will require separate inversion algorithms. As with the FINDS OIL system, there is also an inherent assumption that the dispersed oil plume is constant and homogeneous outside of the sample volume, and that the oil has not been affected by weathering which changes the properties from those registered in the LUT. Finally, as with the FINDS OIL instrument, fouling of the optics in heavier oil concentrations may be a problem.
Detection of Oil in Water Column: Sensor Design

However with the WINDOW system the fouling can be eliminated with a rotating wiper system configured to each optical sensor head.

Although the system could easily be mounted for testing at Ohmsett, it appears that much of the required development and testing of the inversion algorithms and LUT could be pursued much more inexpensively in a laboratory setting (e.g. deploying the sensor in a large tank and checking for accuracy with various oils and oil-material aggregates against varying natural backgrounds).

3.5 Summary

Table 2 summarizes the various advantages and disadvantages of each system discussed above.

Table 2. Summary of system advantages and disadvantages.

<table>
<thead>
<tr>
<th>System</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| NORBIT WBMS | • Acoustic technology is well-developed  
• System is compact, lightweight and easily deployable in-situ  
• Can be set up in multiple ways, set up possibilities increased with more than 1 sonar  
• System appears to be capable of detecting acoustic anomalies in water column suggestive of oil  
• System provides wide area (minimum 3’x3’) coverage  
• System has already been tested at Ohmsett, details of system mounting have been resolved. | • Although system detects acoustic impedance anomalies (possibly oil), the potential for false positives exists  
• There is no indication that the system will be able to determine oil concentration, droplet size or density once positive identification is made  
• Acoustic detection of plumes assumes homogeneity  
• The acoustic imagery requires substantial data processing with subjective analysis by trained operator |
| WET Labs FINDS OIL | • System can positively identify and characterize the oil (aromatic hydrocarbons) it encounters  
• Fluorometry has been previously used in oil detection, ID, and characterization  
• System calibration is straightforward  
• System can be deployed in-situ in a towed housing  
• Data processing, transmission and presentation scheme is well-developed | • Identification and characterization is limited to a limited volume of water sampled via flow-through fluorometry  
• Correlation of sample characterized by flow-through fluorometer to surrounding water column through correlation with secondary fluorescence backscatter sensor has not been fully demonstrated  
• Flow-through fluorometer may foul in heavier oil concentrations  
• Requires towing of sensor along multiple transects to establish oil plume location and areal extent causing time delay in mapping |
| WET Labs WINDOW | • System is compact, inexpensive and portable  
• Uses an existing sensor (ECO-VSF) for light scattering measurement  
• With Look Up Tables it will both identify and characterize the oil  
• Can be deployed by a single individual Testing at Ohmsett is logistically simple | • Detects, identifies and characterizes oil at a single location (no 3’x3’ areal coverage)  
• Fouling in heavier oil concentrations may be problematic  
• Requires towing of sensor along multiple transects to establish oil plume location and areal extent  
• Inversion algorithm development and population of LUT for multiple oil types against varying suspended material backgrounds, and for oil-suspended material aggregates may be complex. |
4 CONCLUSIONS AND RECOMMENDATIONS

The following recommendations are made as to the next steps in the development and testing process for each of the three systems proposed in response to the BAA.

4.1 NORBIT Sonar

- The most important issue with the NORBIT system is demonstrating its ability to positively identify oil. Initial tests of the system reported in the vendor report show that it detected acoustic anomalies for fresh water in salt water, and dispersed oil in salt water (at the Ohmsett test tank), but it is not clear that the second anomaly could be positively identified as oil. For future tests, the sensor should be tested with a range of targets including both entrained globules and dispersed droplets of oil to see if substance discrimination is possible. Because of the wider areal coverage of the sensor and the problems with reflection, such testing will probably have to be done in a larger, unconstrained setting such as Ohmsett, possibly supplemented by field testing in the marine environment (e.g. on natural oil seeps and aggregations of other natural materials such as plankton and seaweed).

- A second issue to be resolved is the presentation and interpretation of the acoustic signal. The imagery shown in the vendor report shows an anomaly of some sort portrayed in two dimensions. Merely delineating the boundaries of the anomaly appears difficult and requires a trained eye. The ideal presentation would be a computer enhanced, 3-D representation of the anomalous plume to allow rapid comprehension of the location and extent of the plume. Data processing and display upgrades of the system to move toward this capability should be pursued prior to further Ohmsett testing, and then demonstrated as part of the tests in the Ohmsett tank.

4.2 WET Labs FINDS OIL

- The flow-through fluorometry technology embodied in the WETStar sensor is technically sound and has been used in other oil detection and identification applications. The ability of the system to characterize oil (determine droplet size, density and viscosity) against natural backgrounds warrants further demonstration, but this is straightforward and can be accomplished in a laboratory setting.

- The ability of the fluorescence backscatter sensor to characterize the hydrocarbon concentration surrounding the towed body for correlation with the WETStar sensor data needs to be more fully demonstrated. It does not appear that this approach has been used before to detect oil in the marine environment. Further demonstration of the capability could be checked at less expense in a flume where the sensor is mounted behind an obstruction (simulating the towed body) such that oil in the fluid is entrained and mixed behind it, and then scanned by the sensor. The ability of the sensor to identify and characterize the oil in test plumes presented to the sensor should be studied and verified. Test plumes should include both entrained and dispersed oil as well as other substances found in the water column.

- After completion of the tests described above, the overall performance of the FINDS OIL system could be tested at Ohmsett to demonstrate overall capability.
4.3 WET Labs WINDOW

- The optical backscatter sensor (like the fluorescent backscatter sensor with the FINDS OIL system) is a new approach to detecting, identifying, and characterizing oil. One type of this sensor has been routinely used to determine the concentration of suspended natural material in the water column, but has not been employed to survey for oil. The system can readily detect the presence of spherical particles in the water column, but its ability to discriminate oil (both droplets and aggregates) from other materials depends on the scattering angles the sensor is able to measure. A sensor able to measure scattering at angles from 10 to 170 degrees (Multi-Angle SCattering Optical Tool (MASCOT)) was apparently able to distinguish the oil at the mid-range scattering angles during lab tests. The ECO type sensor proposed for Phase II testing only uses large angle scattering. The proposed solution lies in development of the comprehensive inversion algorithms and look-up tables (LUTs) described by the vendor. This development should be pursued and demonstrated before testing at Ohmsett.

- Further testing of the system as described above can be accomplished at less expense in a laboratory setting (e.g. in a water flume or mixing tank). Such a facility may already exist in the oil spill R&D community and should be identified. Once the inherent capability of the system to discriminate oil has been verified for different oil types vs. naturally occurring substances, then testing at Ohmsett could be undertaken.
5 REFERENCES

5.1 USCG Internal References: Vendor-Specific Design Reports


5.2 Additional References


Detection of Oil in Water Column: Sensor Design


Lee, K., *Dispersion of Oil released from the Deepwater Horizon MC 252 Oil Spill following Subsurface Injection of Corexit 9500* (undated PowerPoint presentation).


APPENDIX A. RESPONSE TO SUBMERGED OIL

Responding to oil spills on the surface of the water is often a difficult task with recovery rates generally averaging about 20 percent or less of the oil spilled. Responding to spills of submerged oil is far more complex due to the problems associated with operating in an underwater environment where oil is spreading and dispersing in three-dimensions, visibility is limited, deploying divers is dangerous, and recovery equipment must be far more robust and complex than that used on the surface. However, a number of recent spills involving heavier oils that sink below the surface, as well as the subsurface oil encountered in the Deepwater Horizon spill, underscore the need for improving technology for subsurface oil spill response. Discussions of the various causes, scenarios, type of oils, oil fate and behavior, and response actions are provided in a National Academy of Science Report (NAS, 1999) and a recently published compilation on *Oil Spill Science and Technology* (Fingas, 2011).

A.1 Submerged Oil Location and Configuration

Submerged oil can be found in three forms and sometimes in all three forms in a single spill. The first form to consider moving down in the water column is an overwashed oil slick. Overwashed oil occurs in oil slicks located just below the surface where the oil is only slightly positively buoyant so that it is easily covered by water from breaking waves. Although the oil is still readily available for recovery, it is often difficult to detect and map visually from the surface. Airborne surveillance is generally required for monitoring.

Suspended oil is the second form of submerged oil. This occurs where the oil begins to sink from the surface, either because it was negatively buoyant to begin with or has accumulated sediment to increase its density, but reaches a level in the water column where it becomes neutrally buoyant (density of oil approximately equal to that of the surrounding water). This often occurs at a density interface in the water column (pycnocline). The oil will then move at this level with prevailing currents. Often wave action from the surface will help keep the oil entrained below the surface. Detection and tracking of oil in this form is very difficult as it is not visible from the surface and most airborne remote sensing technologies will not penetrate the water column to a significant depth. Recovery is complicated by the poorly defined and often constantly changing location of the oil.

The third form to consider is sunken oil. This is oil that remains negatively buoyant throughout the water column and comes to rest on the bottom. However, even oil that has sunk to the bottom can become intermittently entrained and moved by currents or even roll along the bottom as clumps or droplets. Because the level of the oil is fixed, it can be detected and mapped by divers and underwater cameras. Some progress has been made in developing in-situ remote sensors to detect and map oil in restricted visibility, at great depth or in other hazardous diving situations. Recovery can often be accomplished by divers and/or underwater suction devices.

In addition to the oil being found at different levels in the water column, it can be found in a range of physical configurations including continuous overwashed slicks; suspended streamers, globules, and finely dispersed droplets; and sunken mats, pockets of oil, and droplets, some of which may be hidden by a thin layer of sediment. Each configuration at any of the three levels in the water column will present a unique set of response challenges. In all three forms, detecting, positively identifying, and mapping the submerged oil is critical to taking effective response actions. These options may include containment or diverting the
oil from sensitive resources and infrastructure, closing water intakes, closing shellfish beds and fisheries, subsurface chemical dispersion, and subsurface oil recovery.

A.2 Submerged Oil Scenarios

Submerged oil can result from several scenarios including a damaged vessel at the surface, a sunken vessel on the bottom that is leaking oil, a leaking subsea pipeline and a subsea blowout. For a damaged vessel or barge leaking on the surface (depicted in Figure A-1), the oil will sink if its density is initially greater than the receiving waters, or if it picks up sediment in the water column or by coming in contact with the shoreline or the bottom. Based on USCG investigations, most of the spills involving submerged oil have occurred from vessels and barges.

![Figure A-1. Heavy oil from a vessel submerged in water column. (From National Research Council (NRC), 1999)](image)

The subsea release scenario is depicted in Figure A-2 for a subsea blowout. Light oil released from a subsea blowout would be expected to rise to the surface. How fast it rises depends on how large the oil droplets are and the density of the oil. Larger droplets rise faster; small droplets may take months to rise, and very small droplets may never reach the surface. Oil will be transported horizontally with surf-acre currents as it rises. Oil released along the bottom could also accumulate sediment and organic material and be transported with subsea currents at depth.

Oil may be intentionally dispersed in the water column using chemical dispersants to keep it from reaching the surface. This was the case in the Deepwater Horizon spill where much of the oil released remained below the surface as it was transported over great distances. During the Deepwater Horizon response, Figure A-2 was used to illustrate why it was important to apply dispersant at the well head. When dispersants are added to oil (either at the surface or at depth), the surface tension of the oil is reduced and it forms droplets that mix into the water. Dispersants work using the same principles as kitchen detergents. Dispersed oil is not “dissolved,” but the increased surface area to volume ratio allowed naturally occurring bacteria greater access to the oil molecules so that they could be degraded. As with un-dispersed oil, dispersed oil would not sink unless it was altered by suspended particles.
Dispersing oil at depth, either naturally or chemically, has the effect of breaking up the oil into small droplets within the water column. Because dispersed oil droplets vary in both size and buoyancy, droplets of different sizes take different lengths of time to rise to the water’s surface. Very small droplets, less than about 100 μm in diameter, rise to the surface so slowly that ocean turbulence is likely strong enough to keep them mixed within the water column for at least several months. In the deep ocean, dispersed oil could also encounter “marine snow,” a continuous shower of mostly organic detritus falling from the upper layers of the water column (Deepwater Horizon MC252 Response Unified Area Command, 2010). If subsurface oil is successfully dispersed into small droplets, processes can result in oil remaining in subsurface waters, with horizontal transport potentially many miles beyond the release point.

Smaller amounts of oil may be released from subsea pipeline leaks, or the leaking of oil from tanks after a damaged vessel has sunk to the bottom. Oil arriving at the surface of the water would not be likely to migrate into the sub-surface again unless it was driven into sub-surface layers by wind and wave action (in which case it would refloat when the turbulence subsides), or unless it was altered by encounters with suspended particles.
APPENDIX B.  ACOUSTIC DETECTION OF OIL IN WATER COLUMN

B.1 Acoustic Detection Mechanism

Sonar works by bouncing sound waves off objects. Sound waves transmitted in water may reflect from a substance that has different impedance. Acoustic impedance is a product of the density and sound speed in the medium. Therefore acoustic detection of oil in the water column relies on the differential acoustic impedance of oil compared to that of water.

When sound hits a droplet of oil, the waves scatter in identifiable patterns. The exact extent of what can be discerned depends on the frequency and power of the pulse transmitted. For high concentrations of submerged oil at specific depths, oil in the water column can be qualitatively mapped by commercial fish-finding and echo sounders or by precision sonar survey equipment (NAS, 1999).

In tests performed with fresh water injected into saltwater, NORBIT discovered that the detection of a plume consisting of a huge multiple of small scatters is more reliable using relatively small bandwidth in the acoustic pulses. This is because a low bandwidth pulse has long correlation time, making the likelihood of multiple scatters interacting constructively, more likely (see Figure B-1). This, in general, amplifies the backscattered signal.

![Illustration of sonar interaction with multiple scatterers.](image)

**High bandwidth pulse**  
**Low bandwidth pulse**

Figure B-1. Illustration of sonar interaction with multiple scatterers.

B.2 Data Processing

In order for a sonar system to serve as an oil detection tool, the data received from the sonar must be processed and interpreted. There are different types of processing used, usually based on the specific sonar equipment and target strength differences between the oil and the bottom. Vendors generally design software specifically to work with their systems.
B.3 Advantages

Advantages of acoustic methods include potential utility when water depth or low visibility precludes visual observations, use at night, and the ability to search relatively large areas. Appropriate systems are commonly available at relatively low cost. They are portable, so they can be deployed on boats of opportunity such as Zodiacs, and they have minimal power requirements. Due to their ping rates, they are also capable of collecting data quickly. Multi-beam sonars can be designed to operate at different frequencies. Higher frequencies give better angular resolution. Lower frequencies provide lower resolution but offer additional range. One advantage is that these systems are relatively common and thus their properties and peculiarities are well known.

B.4 Limitations

Disadvantages include cost, limited availability of equipment and operators, slow deployment times in many areas, and potential for false positives in areas where the acoustic signature of the submerged material is similar to that of oil. Acoustic techniques generate enormous amounts of data that generally take several hours or days to process and verify. Expert data interpreters may be needed to interpret acoustic imagery and identify the targeted object or water property. Interpreted results must often be confirmed using direct sampling or other means (ground truth measurements).

B.5 Example

During response to the Deepwater Horizon spill, lower-frequency sonar could not detect oil directly, but it revealed density changes in deeper water that were probably caused by the oil, giving researchers another way to track the spill (Weber et al., 2010). A group of researchers found that frequencies near 200 kilohertz were best for tracking small oil droplets like those in the Deepwater Horizon spill. Using sonar devices on the NOAA ships *Gordon Gunter*, *Thomas Jefferson*, and *Pisces*, Weber and colleagues could tell that the oil plume was not spreading out more than a few kilometers underwater. Unfortunately, the frequencies they used to spot the oil attenuate quickly in water and do not penetrate deeper than 150 meters, preventing the researchers from detecting oil in lower layers of water.
APPENDIX C.  OPTICAL DETECTION OF OIL IN WATER COLUMN

C.1 Fluorescence Mechanism

Fluorosensors are active sensors that rely on the fact that certain compounds in petroleum oils absorb ultraviolet light and become electronically excited. This excitation is removed by the process of fluorescence emission, primarily in the visible region of the spectrum.

Crude and refined oil products are primarily composed of saturated and aromatic hydrocarbons, resins, and asphaltenes. Polyaromatic hydrocarbons (PAHs) are chemical compounds comprised of fused rings containing strong unsaturated bonds. Due to the structural arrangement of PAHs, they tend to fluoresce in response to light energy. Through the process of fluorescence, the light energy that was absorbed by the oil-based compound is released back to the ambient environment, returning the molecules to their original ground state. Despite a difference in molecular structure, alkanes (saturated hydrocarbons) will also fluoresce when exposed to a focused light source.

Various intensities and wavelengths of light can be used to excite PAH and alkane molecules into a state of fluorescence. However, numerous studies have shown that high-energy ultraviolet (UV) light in the wavelength range 200 nanometer (nm) to 400 nm is the most effective source of excitation, yielding the strongest fluorescent emission. PAH compounds responding to UV tend to fluoresce quite distinctly, emitting photons in the visible light wavelength range (400–600 nm: violet to orange), with specific wavelengths of emission serving to identify the types of PAH compounds present. Similarly, alkane molecules will fluoresce in response to UV, but they do so at a lower wavelength outside the visible light spectrum (UV-A bandwidth; 320-400 nm), making them less viable indicators of oil.

C.2 Scattering Mechanism [from Twardoswki, 2012]

Wide angle scattering measures refracted and reflected light off suspended particles and is thus dependent on the size and the refractive index of the particle (or droplet) relative to the surrounding medium. For oil emulsions suspended in natural waters, the refractive index is a close analog to density and viscosity (Vargas and Chapman, 2010). Particles that are most readily detected and quantified with this technique are those that are nearly spherical, namely bubbles and oil droplets, because such particles produce spherical lensing effects characterized by distinct and unique constructive and deconstructive interference patterns in angular scattering, superimposed on smooth, regularly shaped scattering functions from naturally occurring background particle populations. The technique, also called wide-angle-light scattering (WALS), has recently gained significant interest for inexpensive, accurate characterization of particles in several industrial applications, including soot emissions.

Figure C-1 illustrates a schematic of the measurement of angular scattering from a suspended particle population. If particles in solution are separated by at least three times their radii (true in almost all but the most densely populated solutions), then the scattered light received at angle $\theta$ is an aggregated contribution of light scattered from every particle, with each scattered light wave having a phase difference $\sim n(1-\cos(\theta))$. At near forward angles, where $1-\cos(\theta) \approx 0$, there is little phase difference regardless of the particle index, and therefore the total intensity of light received at angle $\theta$ is proportional to $d$. This is the working theory of laser diffraction instruments, one of which, the Laser In Situ Scattering and Transmissometry (LISST)
Detection of Oil in Water Column: Sensor Design

(Sequoia Inc.) has been used in oil spill studies. However, it has limitations in that emulsified oil particles cannot be differentiated from other particles and oil composition (i.e., density) cannot be derived.

Figure C-1. Light scattered at angle $\theta$ by an object of refractive index $n$ and of size $d$ illuminated by an incident light wave of wavelength $\lambda$.
Adapted from Marcos et al., 2011.

At other angles, the difference in phase becomes important, so that the total intensity of scattered light is mostly determined by refractive index, size, and shape. Also, for particles smaller than the wavelength of light, all the scattering is essentially in phase, so size affects scattering at all angles. For natural seawater having a mixture of particles of various sizes, compositions and shapes, this fundamental theory remains the same. It is therefore possible to infer both the size and composition (i.e., refractive index, analogous to density and viscosity) of particles in seawater from measurements of angular scattering. Zhang et al. developed and demonstrated an inversion model capable of characterizing particles from 0.01 to 100’s $\mu$m in a complex natural mixture of particles in the coastal ocean. This technique is readily adaptable to detecting oil droplets amid a variety of natural particles, many of which could have similar sizes.

To initiate the inversion, a library of angular scattering shapes also known mathematically as a kernel function $\beta = [\beta_1, \beta_2, \ldots \beta_M]$ needs to be constructed first, where $\beta_i(\theta)$ is the volume scattering function (VSF) normalized to total scattering $b$. Each $\beta_i(\theta)$ can be considered a scattering signature for a specific particle type such as an oil emulsion, representing the $i$th particle subpopulation among a total of $M$ potential subpopulations in water. With the precompiled library ($\beta$) and the measured VSF $\beta(\theta)$, the equation

$$\beta(\theta) = \sum b_i \beta_i(\theta)$$

is solved for with least-squares minimization using a non-negativity constraint. The solved $b_i$ parameters are the relative scattering contributions for each subpopulation from the library. For a specific type of particle such as an oil emulsion, several subpopulations can be fit from the library, each representing a different size distribution. If $b_i = 0$, then the corresponding subpopulation does not exist. Size distributions and volume concentration of each subpopulation are quantitatively derived by scaling the initial modeled distribution by each $b_i$. Furthermore, since the density and viscosity of each oil emulsion subpopulation is known from its refractive index, mass concentrations are readily computed from volume concentrations.
C.3 Advantages

The required scattering parameters are simple to measure using commercially available scattering sensors with low power light-emitting diode (LED) sources and silicon diode detectors, which can all be packaged in a relatively small container.

C.4 Limitations

Detection using fluorescence has limitations in that emulsified oil particles cannot be differentiated from other particles and oil composition (i.e., density) cannot be derived. Scattering techniques need specialized inversion methods to interpret the results.

The primary limitation of traditional towed fluorometers is that they sample the water column at a specific point and do not provide information on the areal extent of the hydrocarbon contamination measured. Mapping of an oil plume would therefore require multiple transects at different depths through the plume to allow comprehensive mapping requiring a significant amount of time. This is not a problem in a relatively static plume, such as with a continuous subsea blowout or leak from a vessel. But if the plume is transient, its location and configuration may have changed substantially by the time the map image is produced.
Detection of Oil in Water Column: Sensor Design

(This page intentionally left blank.)