Focuses on colloid chemistry phenomena and solutions involved in oil spills and their cleanup

In April of 2010, the Deepwater Horizon oil spill in the Gulf of Mexico became the largest accidental release of oil into marine waters in history, resulting in severe environmental, health and economic consequences. With massive cleanup and relief efforts that followed, the event led many science and engineering communities to apply their expertise and knowledge towards oil spill remediation advancements. Oil Spill Remediation: Colloid Chemistry-Based Principles and Solutions is based on a special symposium run by leading scientists, engineers and policy makers at the 2011 annual SME meeting, dedicated to advancing oil spill remediation technologies.

Divided into three sections, Oil Spill Remediation: Colloid Chemistry-Based Principles and Solutions begins with a science-based overview of the 2010 Deepwater Horizon oil spill. Next, it discusses:

- Oil spill remediation from the perspective of physicochemical and colloidal science
- Current regulations on toxic impact of oil and dispersants, and the available environment assessment tools and resources for the remediation of oil spills
- Current research on dispersants, colloids, and other options for remediation

Each chapter addresses scientific problems associated with current technologies and highlights the urgent need for better remediation methods for oil spills. With contributions from Lisa Jackson (Administrator of the EPA, 2009-2013) and from leading researchers, scientists, engineers, and policy makers, this monograph is a valuable resource for experts and students in, or interested in, the field to understand, design, and develop new and efficient remediation techniques.

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OIL SPILL REMEDIATION
CONTENTS

Foreword vii
Preface ix
Contributors xi

1 Science-Based Decision Making on the Use of Dispersants in the Deepwater Horizon Oil Spill 1
Albert D. Venosa, Paul T. Anastas, Mace G. Barron, Robyn N. Connny, Marc S. Greenberg, and Gregory J. Wilson

2 Understanding and Properly Interpreting the 2010 Deepwater Horizon Blowout 19
by NCEAS Gulf Oil Spill EcoTox Working Group

3 Remediation and Restoration of Northern Gulf of Mexico Coastal Ecosystems Following the Deepwater Horizon Event 59
Michael J. Blum, Brittany M. Bernik, Thomas Azwell, and Eric M.V. Hoek
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Challenges in and Approaches to Modeling the Complexities of Deepwater Oil and Gas Release</td>
<td>89</td>
</tr>
<tr>
<td>5</td>
<td>Oil Films: Some Basic Concepts</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>Johan Sjöblom and Sébastien Simon</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Remediating Oilfield Waste and Spills</td>
<td>161</td>
</tr>
<tr>
<td></td>
<td>Raymond S. Farinato</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Multipronged Approach for Oil Spill Remediation</td>
<td>175</td>
</tr>
<tr>
<td></td>
<td>Partha Patra and Ponisseril Somasundaran</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Packed-Bed Capillary Microscopy on BP-Oil-Spill Oil in Porous Media</td>
<td>189</td>
</tr>
<tr>
<td></td>
<td>Peixi Zhu, Qing Wang, Yuly A. Jaimes-Lizcano, and Kyriakos Papadopoulos</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Jameson Cell Technology for Organics Recovery</td>
<td>221</td>
</tr>
<tr>
<td></td>
<td>Graeme J. Jameson</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Development of Gelling Agent for Spilled Oils</td>
<td>231</td>
</tr>
<tr>
<td></td>
<td>Kazutami Sakamoto</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Microstructures of Capped Ethylene Oxide Oligomers in Water and N-Hexane</td>
<td>247</td>
</tr>
<tr>
<td></td>
<td>Mangesh I. Chaudhari and Lawrence R. Pratt</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Some Colloidal Fundamentals in Oil Spill Remediation: The Water/Surfactant/Hydrocarbon Combination</td>
<td>259</td>
</tr>
<tr>
<td></td>
<td>S. E. Friberg, H. Hasinovic, and Pi Belobrov</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Physicochemical Properties of Heavy Oil–Water Interface in the Context of Oil Removal from Seawater by Froth Flotation</td>
<td>279</td>
</tr>
<tr>
<td></td>
<td>Louxiang Wang, Meghan Curran, Meijiao Deng, Qingxia Liu, Zhenghe Xu, and Jacob Masliyah</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Measurement of Interfacial Tension in Hydrocarbon/Water/Dispersant Systems at Deepwater Conditions</td>
<td>295</td>
</tr>
<tr>
<td></td>
<td>Mohamed A. Abdelrahim and Dandina N. Rao</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Surfactant Technologies for Remediation of Oil Spills</td>
<td>317</td>
</tr>
<tr>
<td></td>
<td>Edgar J. Acosta and Suniya Quraishi</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Role of Structural Forces in Cleaning Soiled Surfaces</td>
<td>359</td>
</tr>
<tr>
<td></td>
<td>Darsh Wasan, Alex Nikolov, and Gopi Sethumadhavan</td>
<td></td>
</tr>
</tbody>
</table>

Index 371
The 2010 Deepwater Horizon oil spill in the Gulf of Mexico ranks among the worst environmental disasters in our history. It claimed 11 lives and interfered with ecological balance, sustainability efforts, and the overall way of life for millions of people. Massive, multipronged, and technologically advanced oil cleanup efforts were launched immediately, and they achieved a remarkable degree of success. But the spill and the cleanup efforts that followed also underscored the scope of the potential for ecological disaster. We still have a great need for technological innovations in this field not only to develop strategies that will prevent another calamity like the Deepwater Horizon spill from occurring but also to strengthen our ability to respond swiftly if that time ever comes.

This issue was the main focus of a symposium organized under the leadership of Professor Somasundaran for the Society for Mining, Metallurgy, and Exploration. The symposium, which I had the privilege of addressing, presented diverse perspectives on the potential use of existing, but as yet unexploited, fundamental scientific principles for developing more effective oil spill remediation technology. The presentations that came out of the conference have been compiled into a monograph titled *Oil Spill Remediation: Colloid Chemistry-Based Principles and Solutions*. They outline the scientific methods, approaches, and plausible routes for the effective and rapid cleanup of spilled oil from sea surfaces, oil-soaked sands, and deep sea, from the perspective of colloid chemistry.
As a former administrator of the U.S. Environmental Protection Agency and a scientist by training, I am delighted to be a part of this endeavor. I am inspired by the dedication that scientists from all over the world have shown in promoting the development of advanced, environmentally safe technology for the quick and effective remediation of spilled oils. I extend my gratitude and appreciation to the authors, editors, and publishers of this important monograph.

_Environmental Protection Agency Administrator, USA_  
2009–2013  

LISA PEREZ JACKSON
Major environmental tragedies generate a host of different alarm responses from different communities. Such events trigger a cascade of actions that include immediate response, long-term remediation, and strategies for preventing similar mishaps in the future. Examples of such tragedies include many oil spills the world over. One such recent major incident was the Deepwater Horizon accident in April 2010 in which massive amounts of subsea crude oil escaped into the marine and nearshore environments due to a drilling rig explosion and blowout in the Macondo Prospect in the Gulf of Mexico. While heroic efforts on the part of first-responders and remediation crews lessened the impact of the spill, it was clear that the technologies available for remediation should be improved. Many science and engineering communities applied their expertise and knowledgebase through the lens of a crude oil spill in an effort to contribute to improve future remediation options. A symposium and subsequently this book arose out of one such effort.

The special symposium entitled “Mineral & Metallurgical Processing: Separation Techniques to Meet Oil Spill Challenges” was run at the 2011 annual meeting of the Society for Mining, Metallurgy, and Exploration (SME) in Denver, Colorado. The intent was to draw upon the expertise of scientists, engineers, and policy makers with an aim to advancing oil spill remediation technology and its use. Both the petroleum and mining industries operate on scales that affect the environment. Sharing expertise related to environmental stewardship seemed both prudent and beneficial. Talks presented during this symposium formed the core of, and provided a platform for, additional contributions that were molded into this book. The various chapters present views from a variety of vantage points—regulatory, first-responder, toxicology, and physicochemical and colloid science. We hope that holding such a diverse collection of perspectives in a single purposeful constellation will provide some light along the path to better remediation technologies.
The chapters address the deeper scientific problems associated with the currently used technologies that have either become evident only in hindsight or were initially thought to be too insignificant for consideration. For example, while skimming booms are used, the possibility of improving absorbing efficiency by manipulating surface rugosity is a new direction that can be potentially pursued. Also, how dispersants can be improved for bettering their performance on the sea surface, under deep sea high pressure and at high-temperature conditions is addressed in this book. Novel methods that will enhance our understanding of oil-dispersant microstructure are explored here via molecular dynamic simulation. How fundamental properties such as surface tension, droplet film stability and coalescence, and accessibility of microbes to oil/sand/water are the key to enhancing the efficiency of many remediation applications is discussed in the context of the usage of dispersants and the physicochemical complexity of sand–water–air–oil systems. A few of the authors have combined insights gained from studies on oil dispersion in microscopic environments with the scaled-up technologies that are used in mineral processing to arrive at solutions for the efficient removal of oil from beach sands. The urgency of the need for better remediation technologies is highlighted in some of the chapters, which outline the environmental impact of the various steps that are typically adopted in oil spill remediation currently. Though all the separation techniques may not have been discussed in detail here, we hope that this treatise will prove valuable for scientists and practitioners as well as for researchers and students venturing into this area, in their quests to understand, design, and develop new and more efficient remediation techniques. We thank D. R. Nagaraj for guiding the development of the symposium and Derek D. Kim, Chi Lo, Yang Shen, and S. Murthy Khandrika for their help with formatting. We express our gratitude toward Lisa Jackson, Administrator of the EPA (2009–2013), for the inspiration and encouragement she unstintingly provided.

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SCIENCE-BASED DECISION MAKING ON THE USE OF DISPERSANTS IN THE DEEPWATER HORIZON OIL SPILL

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1.1 INTRODUCTION

The explosion of the Deepwater Horizon (DWH) oil rig in the Gulf of Mexico on April 20, 2010, led to the tragic loss of 11 human lives. It also unleashed the largest oil-related environmental disaster in U.S. history and the second largest in recorded history.

A failed blowout preventer below the DWH drilling rig caused an unprecedented amount of oil and associated gas to discharge continuously over a period of 3 months. Spill response capabilities were tested to their limits by the continuous and rapid flow of crude oil from the seafloor. Responders turned to information from previous incidents and all available scientific literature to help formulate effective response approaches and deal with unprecedented circumstances.

Lessons learned from the 1989 Exxon Valdez incident in Alaska and other major oil spills have taught us that conventional mitigation techniques such as booming, skimming, and mechanical recovery cannot be fully relied upon to prevent oil from reaching shorelines and damaging sensitive ecosystems during a large-scale spill. They also offer insights into the conditions and circumstances in which dispersant application may be more or less effective. Early in the Exxon Valdez spill, for example, alternative response techniques including the use of dispersants and in situ...
burning were attempted to minimize spread of the surface slick. Four attempts to apply dispersants over the course of 4 days were deemed ineffective due to circumstantial and operational challenges such as equipment failure and lack of sufficient wave action at sea to adequately mix the dispersant with the oil. As a result, dispersant application was discontinued (NRC, 2005).

While all oil spill cleanup techniques have associated environmental trade-offs, those related to the decision to use dispersants may be especially complex. Unlike mechanical recovery, which physically removes oil from the environment, dispersant application drives oil from the surface into the water column. This keeps oil away from shore and transfers exposure risk from water fowl and shoreline species to planktonic and pelagic species. But at the same time, this technique delays eventual removal of oil fractions that are amenable to natural biodegradation processes. In 2005, the U.S. National Research Council acknowledged that, indeed, “one of the most difficult decisions that oil spill responders and natural resources managers face during a spill is evaluating the environmental trade-offs associated with dispersant use” (NRC, 2005).

The depth at sea and continuous flow of oil from the DWH well also posed entirely new challenges for oil spill responders and decision-makers. The point source of discharge was situated approximately 1500 m below the water surface, and oil rising to the surface continued to spread over an ever-increasing area. Subsea dispersant application was raised as a potential response option to overcome these unprecedented circumstances (Kintisch, 2010). There are several practical advantages associated with the application of dispersant directly at the point source of discharge. First, dispersant can be applied directly to fresh oil, before lighter oil fractions are lost and before oil has time to significantly weather and emulsify with water as a result of naturally present surface active agents. Second, direct injection at the point source increases the probability that applied dispersant will encounter all or most of the released oil. This significantly increases efficiency of treatment and decreases the amount of chemical added to the environment. In contrast, a slick on the water surface may be fragmented and stringy, resulting in wasted chemicals in unnecessary quantities when applied from overhead.

Prior to the DWH incident, most (if not all) existing oil spill response knowledge was based on surface spills and surface applications of dispersant. The behavior of dispersants subsea was (and still is) less understood, and previous research had not focused on the duration or quantity of dispersant used during the DWH incident. Recognizing the unique nature of this challenge and response, the U.S. Environmental Protection Agency (EPA) and the U.S. Coast Guard issued a directive requiring BP to implement a monitoring and assessment plan for both subsurface and surface applications of dispersants as part of the BP oil spill response. The goal of the monitoring program was to evaluate daily the effects of dispersant application at the source of discharge. This required an understanding of the fate and transport of dispersed oil. As a result, monitoring efforts were extensive and multifaceted. Coordinated efforts included dissolved oxygen monitoring to ensure hypoxia was not taking place, fluorometric measurements to track the oil plume, laser in situ scattering and transmissometry (LISST) sensor measurements to assess particle size distribution,
oil chemistry analysis of collected samples, monitoring of currents and advective movement of the plume, conductivity/temperature/depth (CTD) profile data collection, and Rototox analyses to estimate acute toxicity from the dispersed plume.

Several government agencies and stakeholders were involved in this monitoring effort, including the National Oceanic and Atmospheric Administration (NOAA), the U.S. Geological Survey (USGS), the Department of Fisheries and Oceans (DFO) Canada, academic researchers funded by the National Science Foundation (NSF), BP response contractors, and the states bordering the Gulf of Mexico. As a result of this collaborative effort, the response community has learned a great deal about subsea dispersion, the behavior of dispersed oil plumes as they advect, how best to monitor oil plumes, and the acute toxicity of certain dispersants. But only those questions immediately relevant to the spill response were able to be addressed in the midst of the crisis and its immediate aftermath. Many more important scientific questions remain. This paper provides the authors’ perspective on deep-sea dispersant injection and identifies what research must be undertaken to answer the questions raised by the DWH oil spill tragedy.

1.2 BRIEF HISTORY AND EVOLUTION OF DISPERGANTS FOR OIL

1.2.1 Spill Mitigation

According to Etkin, 367 of the 408 oil spills that occurred globally in the period 1966–1969 were treated with dispersants (Etkin, 1998). The first recorded use was on an offshore tanker spill in Germany in 1966 (Lewis et al., 1985). Of those, the most well-known major spill where dispersants were used for treatment occurred in 1967 during the Torrey Canyon incident, which spilled approximately 1 million barrels (bbl) of crude oil (144 million l) off the western coast of Cornwall, England. Over 10,000 bbl (1.6 million l) of surfactants (alkylphenols) and solvents (aromatic hydrocarbons) were sprayed onto the slick for 14 days following the release. This resulted in extreme toxicity to marine life due to the toxic nature of the chemicals comprising the dispersant. The toxicity of the dispersant was deemed mostly due to the toxicity of the solvents in the mixture, not the surfactants (NRC, 1985). However, alkylphenols today are known to be endocrine disruptors, which exert their effects chronically rather than acutely and at low concentrations. The Torrey Canyon incident spurred European, American, and Canadian governments to sponsor research programs to develop more effective and less ecologically harmful dispersants and application equipment.

One infamous spill incident where dispersants were used for mitigation was the Ixtoc well blowout off the Gulf of Mexico in 1979, where over 3.3 million bbl of crude oil spewed into the sea over a period of 10 months (for perspective, the DWH spill reportedly spewed 4.9 million bbl into the Gulf over an 87-day period before accounting for containment and recovery (http://www.doi.gov/deepwaterhorizon/loader.cfm?csModule=security/getfile&PageID=237763)). Dispersant use by Mexican officials was reported to be successful, but dispersants were not used in U.S. waters
because the oil was too weathered to expect success (Etkin, 1998). The second-generation dispersants produced in the 1970s were less toxic but also considerably less effective. One of the first of the third generation of dispersants that emerged in the 1980s was Corexit 9527, a product then manufactured by Exxon. Its toxicity was substantially reduced, while its efficacy in dispersing oil into the water column was significantly greater. This was followed by Corexit® 9500 in the mid-1990s, and this dispersant is still the predominant one in supply in much of the United States, being the one most used in the DWH spill. Other dispersants were produced in the 1990s and 2000s, leading to the products currently listed on the National Contingency Plan Product Schedule (NCPPS) (http://www.epa.gov/emergencies/content/ncp/tox_tables.htm# dispersants).

1.3 DISPERSANT EFFICACY AND DISPERSION EFFECTIVENESS

The term “efficacy” is generally defined as the capacity to produce a specific effect under highly controlled conditions. “Effectiveness” describes an effect produced under noncontrolled conditions. In the latter sense, the researcher cannot create a control to use as a comparative baseline. So, when we describe how well a product disperses oil, we use efficacy to describe oil dispersion in a controlled laboratory setting such as a flask containing oil, water, and a dispersant, compared to a control flask containing oil and water but without dispersant. In the field, there can be no control. We describe how effective a chemical disperses oil in the field by taking measurements that may indirectly indicate effectiveness such as particle size distribution, buoyancy, analytical measurements, and fluorescence and then comparing these data to measurements from historical, controlled laboratory experiments.

To be considered for use in the United States as an efficacious oil spill mitigation agent, a dispersant product must be listed on the NCPPS. Listing on the NCPPS is obtained by passing test protocols identified by EPA: the manufacturer must provide data on the swirling flask test (SFT) and standard aquatic toxicity assays. These tests are described in Appendix C, Subpart J of 40 CFR part 300, series 900 (U.S. Environmental Protection Agency, 2003). Listing of a dispersant on the product schedule has been contingent on the dispersant being at least 45% effective in dispersing Prudhoe Bay and South Louisiana crude oils in the SFT laboratory test.

After promulgation of the SFT in 1994, unexpectedly large discrepancies were discovered between the data submitted by product vendors and data generated by EPA contractors (Clayton et al., 1993). The EPA’s Office of Research and Development (ORD) conducted an in-depth laboratory study to determine the cause of this anomaly. The results indicated that a baffled flask provided substantially superior results both in terms of the degree of dispersion and variability among replicates, mainly due to the over-and-under type of mixing induced by the flask’s baffles. Hence, the baffled flask test (BFT) was concluded to be the superior protocol for testing and listing dispersant products on the NCPPS (Sorial et al., 2004a, b). Soon after, ORD began to work with EPA’s Office of Emergency Management to develop a proposed rule that incorporated changes to the existing protocol.
A follow-on study was conducted to develop a pass-fail decision rule. The approach is based on calculating the lower 95% confidence limit from the mean of all replicate measurements that must be greater than a set efficacy level. The higher the variance, the lower is the probability of passing the criterion. This approach ensures that only the most effective dispersants will be selected for inclusion on the product schedule and that a high degree of confidence will accrue in making these decisions. When all the results were in, a more stringent threshold was proposed (Venosa et al., 2002), although ongoing research may suggest that the ultimate threshold may be slightly changed to account for physically dispersed oil.

Although other laboratory testing procedures are available in the literature, the BFT is the only one that has undergone quantitative mixing energy calibration. A hot wire anemometer was used to quantify and compare the turbulence in the baffled flask (BF) and the swirling flask (SF). The velocity gradient and energy dissipation rate were computed based on these measurements. Mixing in the BF was found to be much more uniformly distributed than in the SF. The BF average energy dissipation rate was about two orders of magnitude higher than in the SF. Also, in the BF, the size of the microscales approached the size of oil droplets observed at sea, which means that the turbulence in the BF closely resembles the turbulence occurring at sea during breaking waves (i.e., a moderately energetic sea state). Hence, the BF was deemed preferable for dispersant efficacy (DE) testing in the laboratory (Kaku et al., 2006).

In an effort to better understand the effectiveness of the eight dispersants on the NCPPS that at the time were readily available in the U.S. market, EPA conducted efficacy tests in a laboratory using the BFT in a controlled situation using reference S. Louisiana crude (SLC) oil. Testing was conducted at the two temperatures in the Gulf: 5°C to represent temperature conditions for the deep-sea dispersant injection and 25°C to represent the temperature in the top 5 m where surface application was performed. The BFT was modified to test performance only on SLC oil at the two temperatures and to expand the number of replicates from four to six to increase the statistical power. This modification was designed because only one oil was being tested rather than two. Based on the laboratory findings presented earlier, it appears that only three of the eight dispersants would have provided satisfactory SLC dispersion effectiveness (at a volumetric DOR of 1:25) (Venosa and Holder, 2013). Corexit 9500 was one of the three dispersants giving satisfactory results. This conclusion assumes that the BFT is moderately predictive of field results, which may not be an accurate assumption since other factors (e.g., advection, dilution, and current flow) not testable in a closed flask may play a major role in determining performance in the field.

Dispersion effectiveness is ultimately determined by the dispersed oil droplet size distribution (Darling et al., 1990; Lewis et al., 1985). Droplets < 100 µm in diameter have small rise velocities and tend to remain suspended in the water column. They also become widely dispersed in the water column by turbulent diffusion and are more rapidly biodegraded due to the high surface-area-to-volume ratio (Li and Garrett, 1998). In addition, the oil droplets get surrounded by surfactant molecules, forming swollen micelles or microemulsions, which tend to repel each other, further
reducing the probability of recoalescence. Conversely, large oil droplets with diameters in the hundreds of µm tend to recoalesce and resurface unless strong mixing energy exists to overcome their buoyancy. Therefore, smaller droplets are much more favorable from the perspective of oil spill mitigation. Laboratory and field measurements suggest that for effective dispersion of oil in which the dispersed oil droplets remain suspended in the water column, average droplet sizes have to be less than 50–70µm (Lunel, 1993, 1995).

Unpublished LISST measurements of the dispersed oil plume in the deep sea during the DWH spill at 1100–1300 m below the surface showed that most of the plume consisted of particle sizes ranging from 2.5 to 70µm in diameter. Furthermore, light scattering measurements of water samples collected from that plume displayed the characteristic bimodal distribution typical of chemically—as opposed to physically—dispersed oil (Li et al., 2008a, 2009). This suggests, but does not scientifically prove, that the oil in the deep zone was likely chemically dispersed due to the injection of dispersant into the oil exiting from the riser tube. Although it is plausible that the extreme turbulence of the oil as it exited the well may have caused extensive physical dispersion without the need for chemical dispersant use, review of reported data and information in the literature leads us to determine that it is less likely and that the application of dispersants in the deep sea was successful in dispersing the oil at the source.

1.4 TOXICITY OF DISPERSANTS

1.4.1 Laboratory Testing

The EPA performed two phases of laboratory dispersant toxicity testing during the DWH spill to supplement existing data available on the NCP product schedule. Phase 1 involved testing of eight dispersants using both standard toxicity bioassays with a fish and an aquatic invertebrate and in vitro mammalian cell line assays. Phase 2 of EPA’s testing determined the acute toxicity of the eight dispersants mixed with SLC to two Gulf of Mexico estuarine species. In vitro testing was focused on determining if any of the eight commercial dispersants had estrogenic or androgenic activity, as well as any activity in other biological pathways using a large battery of cell line assays. Overall, no activity was observed in any androgenic assay, two dispersants showed a weak estrogenic signal in one assay, and all dispersants showed minimal cytotoxicity (Judson et al., 2010).

The ecotoxicity testing approach used consistent test methodologies within a single laboratory in assessing the relative acute toxicity of the eight dispersants, including Corexit 9500A (identical to Corexit 9500), the predominant dispersant applied during the DWH spill. Static acute toxicity tests were performed using the mysid shrimp (Americamysis bahia) and the inland silversides (Menidia beryllina). For all eight dispersants in both test species, the dispersants alone were less toxic (LC50s, 3 to > 5600 ppm) than the dispersant–SLC mixtures (0.4–13 mg TPH/l). SLC alone was in general similarly toxic to mysids (LC50, 2.7 mg/l) and
Menidia (LC50, 3.5 mg/l) as the dispersant–SLC mixtures. The results were consistent with data available on the NCPPS and indicated that the toxicity of Corexit 9500A was generally similar to other available dispersants when tested alone and as a mixture with SLC (Hemmer et al., 2011). The results of EPA's dispersant toxicity testing were made publicly available on the EPA Internet site (http://www.epa.gov/bpsspill) and facilitated the EPA administrator's advice and support to the incident commander of the decision regarding dispersant use during the DWH spill response.

1.4.2 In-Field Monitoring

The EPA conducted extensive monitoring of the nearshore environment and communities during the emergency response to the DWH spill that included sampling and testing of marine surface water and sediments. Because EPA recognized early that dispersant usage was an environmental trade-off not to be taken lightly, this monitoring was important because it provided relevant data for detecting any measurable environmental impacts from this usage. Markers of dispersants such as dipropylene glycol butyl ether (DPBE) and dioctyl sulfosuccinate (sodium salt) (DOSS) were included in the chemical analysis, and few detections of these compounds were found in water and sediment samples. All such detections were below aquatic life benchmarks for water that were based on biological effects data (http://www.epa.gov/bpsspill; OSAT, 2010). Toxicity testing associated with samples collected in Alabama, Mississippi, and Florida using estuarine and marine organisms (mysid shrimp (A. bahia), inland silversides (M. beryllina), sea urchin (Arbacia punctulata), polychaete worms (Neanthes arenaceodentata), and amphipods (Leptocheirus plumulosus)) resulted in observed toxicity in one surface water and three sediment samples. However, these findings could not be attributed to the DWH spill because, among many factors, the analytical results did not exceed the ecological screening values, the water samples were negative for petroleum and dispersant analytes, and the observed sediment toxicity was inconsistent across test species and likely due to effects from grain size (Integrated Laboratory Systems, Inc., 2010).

In addition, as a part of the directive issued by the USCG and EPA to BP to implement monitoring and assessment of the subsurface and surface applications of dispersants, daily 24-h acute toxicity testing of rotifers was conducted. Rotifers were exposed to offshore water samples collected near the wellhead and response operations. A critical variable for monitoring the long-term effects of the spill was daily measurements of dissolved oxygen, which would indicate consumption of oil by microbial activity. If DO approached 2 mg/l, which was considered hypoxic in the deep sea, considerations would be made by the Unified Command to suspend dispersant injection at the wellhead. Fortunately, this never occurred. The results from over 1000 sample test results conducted on samples taken from May 29 to August 26, 2010, indicated limited observations of toxicity. Approximately 89% of the samples were not toxic (survival >90%), 10% were marginally toxic (survival range <90 to ≥75%), and 1% showed survival <75%. Collectively, these monitoring results were
helpful for daily decisions on the use of dispersants during the spill, including the reduction in dispersant application rate as the response unfolded.

1.5 MONITORING OF DISPERSANTS ON THE SURFACE AND IN THE DEEP SEA

1.5.1 Monitoring in Surface Waters

Dispersion effectiveness during an oil spill is most commonly monitored using guidance set forth by the nonregulatory Special Monitoring of Applied Response Technologies (SMART) protocols (Barnea and Laferriere, 1999; U.S. Coast Guard, National Oceanic and Atmospheric Administration, U.S. Environmental Protection Agency, Centers for Disease Control and Prevention, and Minerals Management Service, 2003). The protocols establish a monitoring system for rapid collection of real-time, scientifically based information to assist decision-making during dispersant and in situ burning operations. Its primary focus determines if dispersant application is relatively effective or ineffective, where the degree of effectiveness is a secondary focus but is often difficult to address quantitatively in the field. The ultimate objective of SMART is to determine whether or not further chemical dispersion should be carried out during an oil spill.

To meet this objective, relative effectiveness (RE) must be defined. According to the SMART protocol, RE describes the amount of oil that the dispersant puts into the water column relative to the amount of oil that remains in the surface slick. A dispersant is considered “relatively effective” if half the oil is dispersed. Extensive laboratory tests have been conducted to determine the extent of chemical dispersion on various oils, but these studies do not represent real-world conditions for reasons already mentioned. An inherent problem occurs when attempting to calculate this in the field, as plumes and slicks are heterogeneous and patchy and no reliable way exists to accurately measure thickness of either. An added complication is apparent when oil is not from a spill of known volume but from a leak and/or continuous spewing source, making a mass balance of oil challenging (Fingas, 2000). Environmental factors such as conductivity or salinity, water temperature, pressure, sea state, and weathering also influence extent of both physical and chemical dispersion. The extent of these influences is poorly understood in real world situations.

The SMART lays out a tiered, structured approach, where Tier I is reliant on visual criteria from aircraft or ships to confirm the formation of dispersed oil (generally as a yellow- or coffee-colored plume below the water’s surface). This is followed by the Tier II, which calls for real-time fluorometric monitoring of the underwater plume and discrete sample analysis of oil concentrations at 1 m depth. Tier III expands on this and uses additional fluorometers to monitor multiple depths between 1 and 10 m and collection of ancillary environmental data on water temperature, conductivity or salinity, pH, dissolved oxygen, and turbidity. These monitoring techniques are sufficient for the majority of spills although false positives and negatives may occur, affecting confirmation of dispersion effectiveness (Fingas, 2003). Since the establishment of SMART, reviews have highlighted the limitations of the methods (Goodman, 2003) and subsequent updates to the protocols in 2006 and 2008.
1.5.2 Monitoring in the Deep Sea

In the case of the DWH oil spill, the existing SMART protocols, as written, provided insufficient guidance for examining dispersant effectiveness. This was due to the unprecedented nature of the spill, given the extreme depth of the wellhead leak within the ocean. This posed unique challenges to the monitoring efforts, where oil that remained in the subsurface plume (between 1000 and 1500 m) could not be tracked via common methods such as aerial surveys or shallow-towed fluorometers. Tracking during the DWH emergency response effort, therefore, required a modified monitoring approach using vertical profiling packages to extend fluorometric measurements and water sample collection to the deep-ocean floor. Sampling was conducted in a radial pattern to initially confirm the existence and location of a subsurface plume resulting from dispersant application at depth. Added to the measurement suite was a LISST sensor to measure suspended particle or droplet size to indicate degree of dispersion (Li et al., 2007). Since the LISST cannot differentiate between chemical and physical dispersion, multiwavelength fluorescence analyses of discrete samples to calculate fluorescence intensity ratios (FIR) were used (Bugden et al., 2008). Discrete and in situ fluorescence analyses both revealed the presence of what was termed the “fluorescence anomaly” due to elevated values above background natural organic matter in the deep ocean. Although there has been much debate over which fluorometer is best equipped (wavelengths, sensitivity, calibration) to measure dispersed oil, all sensors used during the response efforts were capable of measuring some portion of the oil. Validation of any anomalies was confirmed with chemical analyses (PAHs, TPH, BTEX) during the response effort.

The DWH oil spill possessed both surface and subsurface plume components (Fig. 1.1). The response efforts at the surface were informed by the SMART monitoring program, along with hydrodynamic ocean circulation models and innovative remote sensing techniques (Hu, 2011). At depth, the response effort used various indicators to detect and track the subsurface plume, where assessment was conducted by a collaborative team of scientists from federal, academic, and industrial organizations who were tasked with providing rapid response analysis of data (Joint Analysis Group membership at http://ecowatch.nccdc.noaa.gov/jag). The multi-pronged approach required by the unique demands of the spill calls to light the need for further research in monitoring technologies and the need for updating the living guidance documents that make up SMART.

1.6 Fate and Transport of Dispersants and Dispersed Oil

Understanding the transport and subsequent fate of oil and dispersed oil is important in aiding the decision-making process for response to an oil spill of any magnitude. These processes have a direct influence on the concentration and, therefore, the effects exerted on the ecosystem. The whole strategy behind use of dispersants is predicated on creating tiny droplets of oil, driving them into the water column where exposure of water fowl to the toxic and smothering slick is limited, and rendering the
droplets amenable to more rapid biodegradation due to the high surface area imparted by the dispersant treatment. The use of chemical dispersants also changes the behavioral variation of entrained oil droplets compared to natural dispersion. As pointed out by NRC (NRC, 2005), the movement of oil in the environment involves surface transport (mostly spreading, which determines the shape, thickness, and location of the slick, all of which affect decisions on using dispersants), vertical transport into the water column (which is responsible for the initial dilution after dispersant application), and horizontal transport or advection (which is responsible for the ultimate dilution of the oil mitigating the effect on fish and enhancing its biodegradation).

The EPA in concert with DFO Canada has conducted substantial research in the recent past on the importance of mixing energy in achieving the small particle size distribution needed for permanent dispersion in the bulk-water column (Li et al., 2008a, b). This work was conducted at the wave tank co-owned by EPA and DFO and located at DFO’s Bedford Institute of Oceanography in Dartmouth, Nova Scotia (Li et al., 2008a). In this study, the wave tank was operated in flow-through mode to simulate advective dilution of the dispersed oil plume in the sea. This led to the
development of the term “dynamic dispersion effectiveness” (DDE), which reflects both dispersion of oil into the water column and transport and dilution of the dispersed oil droplets through the water column. Dynamic dispersion effectiveness differs from the DE obtained in bench-scale flask tests, where only the contact efficiency between oil and dispersant is measured in small enclosed surroundings during which unlimited collision frequency between oil droplets and eddies may occur. The flow pattern was clearly different when the wave tank was operated in flow-through mode compared to batch mode. In particular, the backflow near the bottom of the wave tank during batch operation was overcome by the forward current in the flow-through system, which purged the smaller dispersed oil droplets that were suspended in the water column out of the wave tank. This reduced the interdrop collision frequency that would cause recoalescence and resurfacing of the smaller dispersed oil droplets while retaining the larger oil droplets floating at the surface to maintain high droplet–eddy collision frequency for the breakage of droplets into small particles (Tsouris and Tavlarides, 1994).

Figure 1.2 summarizes the effect of dispersant type and wave energy on the average dispersed oil droplet volume mean diameter (VMD) for Alaska North Slope crude oil. In the absence of chemical dispersant (Fig. 1.2a), the oil droplet sizes remained large and highly variable (VMD ~150–400 µm) under the coherent, nonbreaking wave condition but were rapidly reduced in size and variability (VMD ~150–200 µm) under breaking wave conditions. In the presence of the chemical dispersant Corexit 9500 (Fig. 1.2b), the dispersed oil droplet sizes remained large but considerably reduced in variability (VMD ~300 µm) under coherent wave conditions. These sizes were dramatically reduced (VMD ~50 µm) under breaking wave conditions within 10 min and maintained at this small size for the rest of the experiment (Li et al., 2008a). In the presence of Dispersit SPC1000 (Fig. 1.2c), the droplet sizes of the dispersed oil achieved the same low VMD even under nonbreaking waves, although they began recoalescing after 20–30 min, while the chemically dispersed oil droplets remained stable. Once the small particle size is achieved, especially in the deep sea as observed in the Gulf oil spill, the droplets are in effect neutrally buoyant, do not recoalesce, and remain at depth as advection continues to dilute the plume and biodegradation ensues.

1.7 FUTURE OIL SPILL RESEARCH AS A RESULT OF LESSONS LEARNED

It is critical that EPA strengthen its knowledge base and expertise in oil spill response and prevention. As with all environmental protection issues, agency decisions related to oil spill prevention, preparedness, and response must be informed by sound science and research of the highest caliber. The agency ORD has developed a comprehensive oil spill research strategy to fill knowledge gaps, focusing on potential human and environmental risks from oil spills and the application of dispersants, surface washing agents, bioremediation agents, and other mitigation measures. The goal of this strategy is to identify research that would provide environmental managers with the tools, models, and methods needed to mitigate the effects of oil spills in all
environments, emphasizing the coastal and inland environments as summarized in Table 1.1. The research needs identified will fill knowledge gaps in four areas to:

- Develop a better understanding of the impacts of oil spills and dispersant application on the environment
- Develop a better understanding of the shoreline, coastal, and inland environment impacts of oil spills, including nonpetroleum oils
- Develop innovative technologies to mitigate the impact of oil spills
- Address the technical needs of the communities impacted by the DWH oil spill