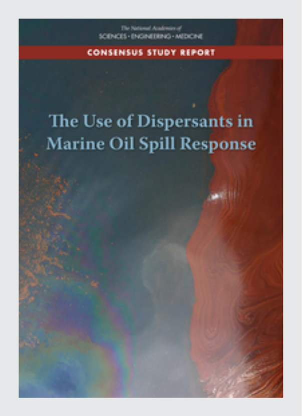

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Committee on the Evaluation of the Use of
Chemical Dispersants in Oil Spill Response

Ocean Studies Board

Board on Environmental Studies and Toxicology

Division on Earth and Life Studies

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This Consensus Study Report was reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise. The purpose of this independent review is to provide candid and critical comments that will assist the National Academies of Sciences, Engineering, and Medicine in making each published report as sound as possible and to ensure that it meets the institutional standards for quality, objectivity, evidence, and responsiveness to the study charge. The review comments and draft manuscript remain confidential to protect the integrity of the deliberative process.

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Although the reviewers listed above provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations of this report, nor did they see the final draft before its release. The review of this report was overseen by **CARYS MITCHELMORE,** University of Maryland Center for Environmental Science, and **RICHARD LUTHY,** Stanford University. They were responsible for making certain that an

independent examination of this report was carried out in accordance with the standards of the National Academies and that all review comments were carefully considered. Responsibility for the final content rests entirely with the authoring committee and the National Academies.

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APPENDIXES

SUMMARY

Whether the result of an oil well blowout, a vessel collision or grounding, a leaking pipeline, or some other incident at sea, each marine oil spill will present unique circumstances and challenges. The oil type and properties, location, time of year, duration of spill, water depth, environmental conditions, affected biomes, potential human community impact, and available resources may vary significantly. In addition, each spill may be governed by policy guidelines, such as those set forth in the National Response Plan, Regional Response Plans, or Area Contingency Plans. To respond effectively to the specific conditions presented during an oil spill, spill responders have used a variety of response options, including mechanical recovery of oil using skimmers and booms, in situ burning of oil, monitored natural attenuation of oil,[1] and dispersion of oil by chemical dispersants. Because each response method has advantages and disadvantages, it is important to understand specific scenarios where a net benefit may be achieved by using a particular tool or combination of tools.

Typically, oil spill response tools are used to reduce the amount of floating oil at the surface through direct removal (skimmers), in situ burns, or dispersion into the water column. Floating oil may pose health risks for people (especially spill responders) as well as for seabirds and air-breathing marine species such as sea turtles and marine mammals. Winds may drive floating oil ashore into vulnerable habitats such as salt marshes where oil cannot be removed without causing additional damage. The primary objective of dispersant use is to reduce the amount of floating oil by promoting the formation of small droplets that remain or become entrained in the water column, where they are subjected to greater dissolution and dilution. Under conditions conducive to microbial growth (e.g., the presence of oxygen, adequate nutrients, and sufficient microbial seed population), the small droplets formed by dispersants may also biodegrade more rapidly.

This report builds on two previous National Research Council (NRC) reports on dispersant use (NRC, 1989, 2005) to provide a current understanding of the state of science and to inform future marine oil spill response operations.[2] The response to the 2010 *Deepwater Horizon* (DWH)

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[1] Monitored natural attenuation refers to tracking the environmental processes that break down oil, including biodegradation.

[2] Since the release of the prepublication version, the text was edited for clarity and references have been checked and modified as necessary.

spill included an unprecedented use of dispersants via both surface application and subsea injection. The magnitude of the spill stimulated interest and funding for research on oil spill response, and dispersant use in particular. This report considers and synthesizes much of that work, as well as other literature, to address the Statement of Task (see Chapter 1). Furthermore, the focus of this report is on marine oil spill scenarios for which dispersants would be considered a potential response option. In the United States, that is limited to areas beyond 3 nautical miles from shore and in depths greater than 10 m. Although the focus of this report is spills occurring off the coast of the United States, the expectation is that the report will have broad application internationally.

OIL SPILL RESPONSE DECISION MAKING

Human life is the first priority in marine oil spill response. Hence, the Federal On-Scene Coordinator and Area Contingency Plans place top priority on decisions affecting human health and safety. After human safety, the next priority is development of a response strategy that most effectively reduces environmental consequences, offers the greatest protection, or promotes the fastest recovery.

Determining whether the use of dispersants is appropriate for a given oil spill scenario requires decision-making tools for assessing the relative benefits of the various response options. These tools incorporate available information to estimate the likely fate and transport of oil and dispersant components and to assess the effects associated with human and environmental exposure to oil and dispersant components.

A number of approaches, collectively known as Net Environmental Benefit Analysis (NEBA), help decision makers select the response option(s) most likely to minimize the net environmental impacts of oil spills. NEBA must account for the variable nature of oil spills and a broad range of natural resources that could be impacted. This requires flexibility to allow for "real-time" alignment with changing field conditions.

Three tools that could be used to support the NEBA approach for oil spills are described:

- Consensus Ecological Risk Assessment (CERA): uses a detailed, semiquantitative risk ranking square to perform comparative analyses of response methods;
- Spill Impact Mitigation Assessment (SIMA): similar to CERA, but utilizes a single score for extent of exposure and duration of recovery and adds a weighting factor for resource values based on local priorities established through a stakeholder consensus-building process; and
- Comparative Risk Assessment (CRA): uses an integrated model to simulate the fates and effects of a spill scenario and employs a weighting function to represent the relative exposure, susceptibility, and importance of resources.

Each process involves a structured approach used by the response community and stakeholders to compare the impact mitigation potential of the available response options.

All three decision-making tools (CERA, SIMA, and CRA) have value for supporting contingency plan development, strategic planning during the initial stages of a spill response, or tactical execution during the active phase of a response. Because a CRA relies on an integrated model adapted for a particular spill scenario, it takes considerable time before results are available; hence, it typically has more value for contingency planning. An integrated model consists of various sub-models that simulate the transport, degradation, mitigation efforts, and ultimate fate of the hydrocarbon, and in some cases, the model may even use this information to estimate the effects on important components of the local biota. With further development, the NEBA process also could be used to estimate human health and socioeconomic impacts. Because CRAs evaluate the *relative* risks and benefits of various response options, there is greater tolerance for uncertainties in the modeling. Importantly, each tool can be used to engage stakeholders, an essential element for providing input on local or regional priorities, expanding awareness, and building confidence and trust in the decision-making process.

Recommendation: Decision makers should further evaluate surface and subsea spill scenarios using NEBA tools (i.e., CERA, SIMA, or CRA) to better define the range of conditions (e.g., oil type, sea state, depth, location, resources at risk) where dispersant use may be an appropriate and/or a feasible response option for reducing floating oil.

Although CERA and SIMA can be adapted for situations in which limited information is available to inform the analysis, all tools used in the NEBA process rely to some extent on the ability to estimate both a series of processes that influence where the oil goes and how oil composition changes over time (fate and transport) as well as the effects of oil on species throughout the affected ecosystem (aquatic toxicology and biological effects). The report is organized to first address the state of the science related to fate and transport followed by aquatic toxicology and biological effects. It then covers the human health considerations that are critical concerns for decision makers. Based on this information, the report discusses the trade-offs associated with dispersant use versus other response options under various spill conditions and explains how these trade-offs are weighed using the NEBA approaches described above.

FATE AND TRANSPORT OF DISPERSANTS AND OIL

Fate and Transport of Dispersants

Modern dispersant products (e.g., Dasic Slickgone NS, Finasol® OSR 52, Corexit® EC9500A) are a mixture of solvents and surface active agents (surfactants) with different physicochemical properties and therefore potential fates in the environment. Once released into the aquatic environment, dispersants are subject to rapid dilution, dissolution, biodegradation, and photodegradation processes. Consequently, there is just a brief time window in which ocean biota might encounter the full dispersant formulation. When a dispersant is introduced at depth by subsea injection, dispersant components will differentially dilute and dissolve, with some being retained at depth (e.g., in intrusion layers and sequestered in sediments). In this situation, deepwater[3] biota could be exposed to dilute concentrations of the more persistent and water-soluble dispersant components, such as the anionic surfactant dioctyl sodium sulfosuccinate (DOSS).

In laboratory experiments, dispersant components (including the solvents and surfactants) degrade rapidly, within hours to days. In field conditions, the few studies on the effects of dilution on dispersant fate and transport have shown that concentrations of dispersants reach a maximum of 5-13 parts per million (ppm) after surface applications and generally decrease to less than 1 ppm within minutes to hours.

Research examining the long-term fate of dispersant constituents indicates that only trace amounts of DOSS persist, even after the large volumes of dispersants used in the DWH spill. This indicates that dilution, dissolution, biodegradation, and photodegradation likely acted in that case to limit the long-term exposure of aquatic species to dispersant components.

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[3] The committee recognizes there are varying definitions for the terms “deep water” or “deep-water,” which largely depend on the context of their use; however, for the purposes of this report, the committee generally considers “deep water” to be greater than 500 m.

Fate and Transport of Untreated and Chemically Dispersed Oil

Many types of oils, including crude oil and refined products, may be released into the marine environment, at which point their composition begins to change. The oil type or chemical composition determines the long-term behavior of oil as modified by such processes as evaporation, aerosolization, photochemical oxidation, dissolution, biodegradation, aggregation, and adhesion. Key determinants of physical behavior include the molecular weight distribution of hydrocarbons, the abundance of other elements (e.g., N, S, and O), and the relative abundance of saturates, aromatics, resins, and asphaltenes. The oil's chemical composition also influences the action of dispersants: lighter oils are more dispersible, while dispersants may have limited effectiveness on high-viscosity oils.

Subsurface Transport

In a deepwater blowout, release of gas bubbles and oil droplets creates a buoyant, multiphase plume. As the plume rises, gas bubbles and soluble oil components dissolve into the entrained seawater, decreasing the buoyancy of the plume. A lateral intrusion layer forms, enriched in hydrocarbons, where the dissolved components and microdroplets[4] encounter currents and the ambient density stratification of the water column (see Figure S.1).

Surface Transport

On the sea surface, oil slicks become dispersed through the action of breaking waves. While this occurs naturally, it can be amplified by the application of dispersants. The small droplets formed by dispersion become entrained below the surface by waves, turbulence, and Langmuir circulation.

Droplet Size

Oil droplet size is a primary determinant of both subsurface and surface oil transport; hence, understanding the dynamics associated with droplet formation, size distribution, and transport is foundational for improving studies of oil fate, including the effects of dispersants. Dispersants lower the interfacial tension of oil, thereby promoting the formation of small droplets and microdroplets. With regard to surface oil, droplets form when turbulence drives oil beneath the surface. The depth of penetration and the resurfacing time depend in part on the droplet size. In a deepwater release, droplets form at the source and rise through the water column as a function of their size. Oil type and the densities of the oil and surrounding seawater will influence rise velocity, but generally, larger droplets have greater buoyancy and hence rise more quickly than smaller droplets.

Because of their slower rise rate, smaller oil droplets will lose more soluble components before surfacing and thus release fewer volatiles to the atmosphere. Smaller oil droplets may also be transported further from the source and surface over a broader area, potentially reducing atmospheric concentrations of volatiles. This has implications for oil spill response because inhalation of volatile organic compounds (VOCs) is a major health concern for responders working in the area of the spill. Furthermore, under favorable conditions, small droplets may enable greater biodegradation to occur because of the increased surface area and longer residence in the water column. In the case of microdroplets, insufficient buoyancy prevents their surfacing, and they become trapped at depth with the soluble oil components. The purpose of using dispersants is to enhance the formation of these small oil droplets and thereby increase dissolution and biodegradation while decreasing exposure.

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[4] The committee recognizes that the term "microdroplets" is loosely defined, but in this report the term typically means droplets that are approximately 70 microns or less.

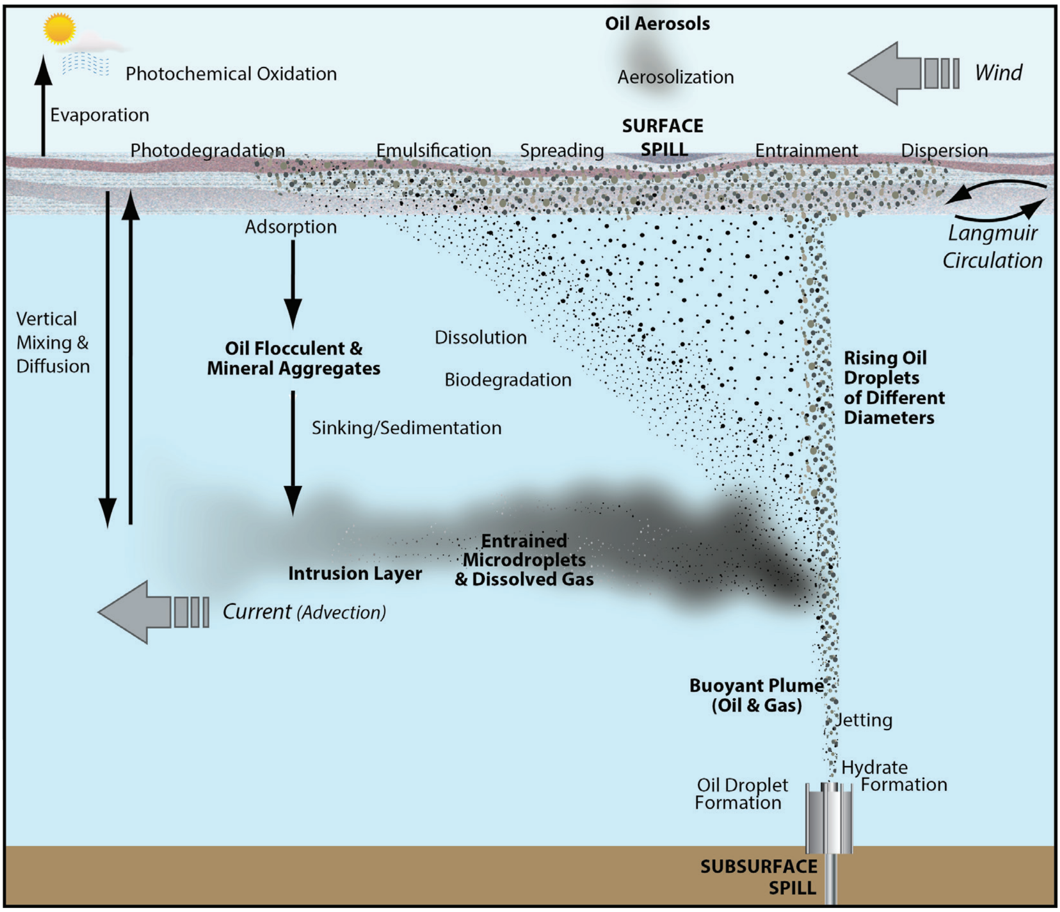

FIGURE S.1 Summary of the important components (bold font) of an oil spill and the processes (normal font) that affect them. Dispersants may exert an influence on all processes shown except for jetting, wind, current, and Langmuir circulation. Surface gravity waves are not explicitly shown for the sake of clarity. SOURCE: Modified from Hazen et al., 2016.

Droplet Models and Experiments

Models of droplet formation and transport have been developed to improve predictions of the fate of spilled oil and effects of dispersants. Experiments and models can provide insight on droplet formation and distribution. For example, models can explore different spill scenarios by varying parameters such as oil properties, flow rate, depth, or the dispersant-to-oil ratio (DOR). Experiments can test how well models perform at different scales and can examine the effects of various oil types, proportions of methane, dispersant formulations, and DORs. The combination of experiments and models provides a powerful tool for understanding factors that determine droplet size and behavior as well as the sensitivity of a system to certain parameters and processes.

For any particular spill, unforeseen factors may impact droplet size and complicate reconstruction of the actual conditions. Field trials and actual spills (spills of opportunity) could help reveal processes that influence oil fate and transport beyond those incorporated into current models and laboratory experiments.

Since the DWH spill, models have been developed to better represent the processes determining droplet size and transport for both surface and subsurface spills. However, sources of uncertainty remain, including processes such as tip streaming, pressure gradients, and out-gassing. Therefore, additional modeling and field-scale experimentation will be required for more accurate predictions of oil fate and transport. Because it can be difficult to obtain permits for experimental field studies, a spill of opportunity is another option for obtaining the observations necessary to improve models. A spill of opportunity involves being prepared and coordinated in advance so that should a spill occur, scientists are in a position to collect samples and data. Any field-scale study will be inherently restricted because of logistical challenges and open boundaries. Thus, it would be highly desirable to develop a large-scale laboratory facility with the ability to include high ambient pressure and observation of droplets as they evolve over time.

AQUATIC TOXICOLOGY AND BIOLOGICAL EFFECTS

Oil can present an immediate hazard to ocean life, both at the surface and below. At the surface, oil can harm animals such as seabirds, turtles, and marine mammals through physical smothering from direct contact, ingestion, inhalation, and aspiration of oil. Dispersants have been used in part to reduce the hazards of surface oil, both at the offshore site of the spill and through wind-driven transport to nearshore habitats. However, the action of dispersants in a surface spill increases the amount of oil in the water column, both as dissolved oil constituents and as small droplets, where fish and other species may be exposed through absorption or ingestion.

Concerns over the substantial use of dispersants during the DWH spill triggered an expansion of research on the toxicity of oil, dispersed oil, and dispersants. Toxicity studies have been conducted by exposing biota to various oil and oil/dispersant mixtures under laboratory conditions. In most experiments, the conditions in the laboratory are not designed to be analogous to conditions in the field. Instead, the experiments are designed to identify threshold concentrations for a variety of marine species to evaluate potential effects of dispersant use on water column species.

However, the results of laboratory studies have been equivocal, due—at least in part—to a lack of consistency in the media preparation, exposure procedures, and chemical analyses, despite earlier recommendations to employ standardized toxicity testing protocols (NRC, 2005). This lack of consistency has reduced the ability to compare results across studies and develop a comprehensive picture of the toxicity of oil and dispersants. As described below, the committee suggests an approach for using results from many studies to develop a coherent analysis of the toxicity of dispersants and chemically dispersed oil.

Dispersant Only Toxicity

Modern dispersants (e.g., Dasic Slickgone NS, Finasol® OSR 52, and Corexit® EC9500A) have been formulated with less toxic chemical constituents, employing ingredients found in common consumer products such as cleaners and cosmetics. However, lack of full disclosure of substances comprising the dispersant formulations following use in the DWH spill contributed to public concern about toxicity, although the Centers for Disease Control and Prevention released the statement that the "ingredients [of Corexit® 9500A and Corexit® 9527A] are not considered to cause chemical sensitization; the dispersants contain proven, biodegradable and low toxicity surfactants."[5]

Toxicity is a function of both concentration and exposure duration. Based on operational dispersant application rates at the surface, the dispersant-only concentrations (i.e., from a

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[5] CDC, 2010.

noncontinuous dispersant application) are expected to range between 1 and 15 mg/L in the first minutes to several hours. Species sensitivity analysis, based on toxicity tests of dispersant alone, yielded an HC5[6] at 65.8 mg/L when field conditions were simulated with a spiked flow-through test (~2.5-hour half-life). Hence, under field conditions with possible exposures of a few hours, the dispersant concentration would be roughly 10-fold lower than the level that would be toxic to the most sensitive 5% of tested species. As underscored in the previous NRC reports, the concern with dispersant use is whether dispersed oil is more toxic than untreated oil is, not the toxicity of current dispersant formulations.

Dispersed Oil Toxicity

To determine the relative toxicity of dispersed oil, many laboratory studies have compared solutions of oil equilibrated with seawater to oil and dispersant mixtures equilibrated with seawater. Toxicity testing protocols consist of three main elements: media preparation, exposure, and chemical characterization. Preparing a dose of oil (media preparation) is not as simple as preparing a dose of a single miscible compound, because oil components vary in solubility and partition into both the oil and the aqueous phase. Two different methods have typically been used for preparing a range of concentrations: variable loading and variable dilution.

Variable Loading

In this approach, a water-accommodated fraction (WAF; aqueous phase separated from the oil after mixing) is prepared for each concentration of oil to be tested: for example, 100 mg oil/L. When a dispersant is included, a chemically enhanced water-accommodated fraction (CEWAF) is produced at the same oil concentration. Both WAFs and CEWAFs contain microdroplets, but CEWAFs contain a higher concentration of microdroplets for the same initial loading of oil. WAF and CEWAF have the same dissolved oil concentration because at equilibrium the dissolved concentration depends on the oil-to-water ratio, not the amount of oil present in microdroplets. An analysis using available variable loading toxicity tests comparing CEWAFs to WAFs shows that the higher concentration of microdroplets in the CEWAF does not increase toxicity until the oil loading is above approximately 100 mg oil/L. Hence, variable loading experiments indicate that at or below approximately 100 mg/L, dispersed oil is no more toxic than is untreated oil. Above approximately 100 mg oil/L the increase in toxicity with dispersants is due to increased generation of oil microdroplets.

Variable Dilution

An alternative approach, commonly applied in oil toxicity tests, uses a single stock solution prepared at a high oil loading that is serially diluted to create a set of decreasing concentrations. However, there is a fundamental problem with this test design. When the WAF or CEWAF is diluted, the concentration of the dissolved oil components decreases and is no longer in equilibrium with the oil in the microdroplets. This causes further dissolution of oil components from the microdroplets until the solution reaches equilibrium. However, the dissolved concentration will be higher than predicted by the proportion of the dilution. Because dispersants create more microdroplets, the dissolved concentration in the CEWAF dilutions will be higher than in the equivalent WAF

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[6] Acute HC5 refers to the concentration at which 5% of the tested species have their LC50 (concentration lethal to half of the test population for a 96-hour exposure). At this or lower concentrations, 95% of the species have an LC50 above the HC5. Note that toxicity is greater when the LC50 or HC5 is lower.

dilutions. This mismatch in the dissolved oil concentrations and composition can be corrected by direct measurement of the dissolved oil concentration in each dilution. However, without correction for the actual dissolved oil concentrations, a direct comparison of WAF and CEWAF toxicity will not produce meaningful results.

Recommendation: Funding agencies, research consortia, and other sponsoring groups should require that research teams use standardized toxicity testing methods, such as those developed by the Chemical Response to Oil Spills: Ecological Effects Research Forum (CROSERF) program, and analytical chemistry protocols to fully characterize hydrocarbon composition and concentrations in the exposure media. For testing the effect of dispersant, the variable loading test design is recommended.

Effect of Exposure Time

The duration of the exposure is another determinant of toxicity.[7] The typical progressive decrease in LC50 for tests of 24-hour, 48-hour, and 96-hour duration indicates that toxicity increases with longer exposure times. In addition to acute mortality, sublethal effects affecting early life stages and adults can reduce fitness and species abundance. Acute and chronic tests typically employ different endpoints: mortality for the acute tests, and growth and reproduction or other endpoints for chronic tests. The lower toxicity thresholds for acute and chronic effects arise from both longer exposure time and the difference in endpoints. Nevertheless, this wide variation needs to be considered when evaluating oil toxicity.

Phototoxicity

Another consideration for assessing the use of dispersants is phototoxicity. Exposure to sunlight enhances the toxicity of certain polycyclic aromatic hydrocarbons (PAHs) absorbed by the organism. The result is a 10- to 100-fold increase in toxicity for these photoactive PAHs. Hence, a reduction in the amount of oil at the surface with dispersant use would lower the potential aquatic toxicity of the oil. Exposure to sunlight also increases the rate of photodegradation, which can affect the resulting toxicity by producing new compounds. Both of these effects need to be considered when assessing the effect of exposure to sunlight. Typically, short-duration toxicity tests do not consider phototoxic effects.

Determining Effects of Dispersant Use

To compare the toxic effects of untreated and chemically dispersed oil on marine life, it is necessary to evaluate the following four factors:

1. Concentration exceeding known acute or chronic toxicity thresholds for the specific oil;
2. Duration of exposure above toxic thresholds;
3. Spatial and temporal distribution of marine life; and
4. Species sensitivity to oil exposure above the acute or chronic toxicity thresholds.

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[7] "Acute" exposure typically refers to an exposure of 96 hours or less. "Chronic" exposures are longer and, in some cases, span multigenerations of the organism. LC50 refers to "lethal concentration" causing 50% mortality of the tested organisms. The term "acute test" denotes a short duration test with mortality as the endpoint. A "chronic test" is a longer duration test usually with sublethal endpoints, although chronic mortality is also observed in these tests.

In addition, it is necessary to quantify the toxicity of the mixture of the dissolved hydrocarbons of crude oil that result during an oil spill. The necessary parameter is the toxic unit (TU): TU equals the ratio of the dissolved aqueous concentration of the compound to the toxic concentration, either LC50 or HC5, of that compound. It has been shown that the toxicity of a mixture of the dissolved hydrocarbons can be estimated by adding the TUs of each component. If the sum of the TUs is greater than one, the mixture will exhibit the toxicity of the level of the LC50 or HC5 used to define the TU. Because TUs are based on the composition of the mixture, it is possible to compare the toxicity of various mixtures of PAHs from different source oils and from mixtures that results from the differential solubility of oil constituents in seawater. Because PAHs vary widely in toxicity, the TU provides a more accurate measure than do the more commonly reported total PAHs, which represent the sum of the PAH concentrations without the LC50 or HC5 normalization.

Recommendation: The use of toxic units should be integrated into revised oil toxicity testing standards, evaluation criteria for models, and response option risk analysis. This represents a paradigm shift away from developing toxicity tests that attempt to reproduce field exposure conditions and toward developing a consistent means of using toxicity metrics such as HC5 and LC50 for toxicity models used with fate and transport models to compare the exposure and toxicity of various response options, including dispersants.

HUMAN HEALTH CONSIDERATIONS

Human health and safety represent the first priority in oil spill response decision making. Surprisingly, significant research effort on the direct human health impacts of oil spills is relatively recent, beginning with the *Exxon Valdez* and *Sea Empress* oil spills and expanding after the *Prestige* oil spill in 2002. The potential health effects of dispersant use during oil spills were not subject to epidemiological investigation until the DWH spill in 2010.

The key questions with regard to human health are whether dispersant use alters the health risk imposed by an oil spill by (1) dispersant use directly causing adverse effects, (2) effects of dispersant and oil mixtures, or (3) indirect effect of dispersant use changing the extent or duration of the spill.

During oil spill response, primary exposure pathways of concern are inhalational and dermal exposure of response workers. Direct effects on response workers can be mitigated through a proper worker health and safety program that focuses on personal protective equipment and monitoring. Community health concerns arising from exposure to oiled shorelines; socioeconomic effects, such as disruption of commercial and subsistence fisheries; and concerns over contaminated seafood also need to be considered as factors in oil spill response.

Human Exposure and Toxicity of Oil

With regard to human exposure to crude oil, the primary oil constituents of concern are the VOCs (benzene, toluene, ethylbenzene, and xylene [BTEX]) and PAHs. The carcinogenicity of benzene and PAHs, particularly benzo(a)pyrene, is well characterized. Dispersants may affect exposure to these oil constituents by altering their fate, transport, and biodegradation. Far less is known about the potential toxicity of weathered crude oil, which has much lower concentrations of the lower molecular weight components of concern, but it is reasonable to consider that it should be lower than the toxicity of fresh oil.

In addition to exposure to VOCs at the response site, VOCs released during an oil spill can contribute to the formation of secondary air pollutants, such as ozone, which could lead to inhalational exposure downwind from the spill location. In a deepwater blowout, subsea use of dispersants could reduce the potential for inhalational exposure by increasing the dissolution of VOCs during the slower transit of dispersed oil droplets to the surface.

Dermal exposure to oil constituents has been shown to cause skin irritation and skin cancer (EPA, 2017). At present, there is insufficient evidence to determine if dispersant use increases the transdermal absorption of crude oil components.

Although responders could be exposed to oil and/or dispersants through accidents or improper use of protective gear, broader community exposure to dispersants or dispersant-oil mixtures is much less likely because dispersant use is limited to offshore spills. Possible routes of exposure include ingestion, inhalation, and dermal contact. Exposure via ingestion could occur through consumption of seafood contaminated with PAHs or dispersant components during or after an oil spill. Protocols for closing and reopening fisheries during and after an oil spill are designed to protect public health from this exposure route.

If a response tool, such as dispersants, shortens the intensity and duration of response activities, and proper health and safety measures are in place, exposure risk would be lower, particularly for responders. This factor merits inclusion as part of the trade-off considerations with regard to decisions on dispersant use.

Assessment of Exposure to Workers and Community Members

To date, exposure assessment during oil spills has been hampered by the lack of protocol development and hence unknown baselines for the constituents of oil and dispersants. To improve assessments of exposure, a standardized, analytical chemistry protocol will be needed to monitor the levels of dispersant components and dispersant-oil mixtures in environmental media and biota in advance of the next spill.

Epidemiological Studies

Two studies of DWH spill responders have attempted to disentangle the direct effects of dispersants from other worker health risks. While these studies noted similar adverse effects associated with dispersant exposures, both have limitations in their ability to validate exposure to dispersants based on self-reporting by workers.

Investigators from the National Institute of Environmental Health Sciences and collaborative programs attempted to assess the impact of exposure to dispersants based on respiratory, dermal, and eye irritation symptoms previously reported as part of an extensive health study of DWH response workers. The second study consisted of a cross-sectional evaluation of 4,855 U.S. Coast Guard personnel involved in the DWH response.

In both of these epidemiological studies, limitations in the exposure assessment for dispersants affect the strength of the conclusions. The delayed initiation of the studies and the lack of a dispersant/dispersed oil biomarker necessitated reliance on self-reporting, making it difficult to accurately estimate exposures and thus the effects of dispersant/dispersed oil versus untreated oil.

Indirect Human Health Effects

Often, the adverse health effects noted in studies of communities near an oil spill, including the DWH, have been associated with psychosocial and economic impacts rather than toxicity associated with direct exposure to chemicals. Communities at particular risk are those that already have relatively poor health and a past history of environmental injustice, which characterizes many of the communities affected by the DWH disaster. Health impacts in both workers and community members likely are at least partly dependent on the duration of the oil spill recovery period. If dispersants shorten this duration, presumably overall impacts on worker and community health would lessen. A spill can also lead to prolonged closure of fisheries, causing secondary effects on community psychological and socioeconomic well-being.

Recommendation: Selection of biomarkers to improve human exposure assessment should consider the toxicity of dispersant and oil components and degradation products (produced by both biological and photodegradation), persistence in the environment, and bioaccumulation potentials. Biomarkers and analytical protocols should be established for each dispersant formulation listed on the U.S. Environmental Protection Agency's (EPA's) National Contingency Plan Product Schedule.

Recommendation: In advance of the next significant oil spill, the reporting requirements for details of injury and illness reporting for worker health and safety should be improved, with a clear focus on whether workers were exposed to dispersant. To that end, publication and ready availability of well-defined DWH worker health and safety statistics is needed. Exposure assessment and toxicological evaluation should recognize that response workers may not be from a healthy worker population and may not know how to minimize exposure.

SELECTION OF RESPONSE OPTIONS

Making the best decision possible during an oil spill requires balanced consideration of the potential consequences of the spill under a natural recovery scenario versus the consequences associated with each response strategy. It can be difficult to make trade-off decisions during an ongoing spill based on field data because observations may be limited. Efforts to ensure human safety, contain the oil, and minimize environmental damage take priority over monitoring and scientific studies. Pre-spill planning and scenario development prior to a spill provide the knowledge base on which decisions can be made during a spill event, as long as human health considerations are included in the NEBA tools as discussed above.

The primary response options considered in this report include surface dispersant operations, subsea dispersant injection, at-sea mechanical recovery, controlled (in situ) burning, biostimulation, and monitored natural attenuation. Typically, a response strategy will require a combination of response methods to adapt to constraints presented by the oil type, physical environment, weather, and health and safety considerations. The advantages and limitations of various response options have been described in detail elsewhere, including previous NRC reports; consequently, this discussion focuses on dispersants.

Surface Dispersant Operations

Dispersants can be applied to surface oil from vessels or aircraft. Aerial application allows for a high coverage rate and for treatment of large volumes of oil. Potential advantages include reduction of VOCs at the surface, no requirements for storing recovered oil, low manpower requirements, enhanced biodegradation, and application to a wide variety of spill situations. A disadvantage is the limited time frame for dispersant application; there is a relatively short "window of opportunity" for treating the spilled oil before it weathers and may become too viscous. Also, aerial dispersant operations are limited to favorable weather conditions, daylight hours, and sufficient turbulence (from waves) to mix the dispersant into the oil, although the operational window for use is expected to be broader than for mechanical containment and recovery techniques. Surface dispersant use requires specialized equipment and expertise as well as special approvals and meeting regulatory requirements.

Subsea Dispersant Injection

A notable advantage of subsea injection is the increased efficiency in treating large volumes of oil, thus requiring less dispersant compared to surface applications. At depth, dispersed oil will be subject to greater loss of soluble components and increased dispersion than will oil treated through surface application of dispersant. Furthermore, subsea injection operations can take place continuously, while surface application is limited to daylight hours and favorable wind and sea state conditions. Subsea injection requires less manpower than other response options and may reduce the VOCs at the surface.

As with other response options, there are potential limitations and trade-offs associated with subsea dispersant injection. Like surface application, subsea dispersant injection requires special approvals, is subject to regulatory requirements, and requires specialized equipment and expertise. It is more difficult to monitor dispersant effectiveness in the subsea than at the surface. Furthermore, by entraining oil within the water column, it may have greater impacts on marine biota present in the water column. In addition, less is known about the long-term effects of subsea dispersant injection.

COMPARATIVE STUDIES OF RESPONSE METHODS

A limited number of comparative studies have evaluated the effectiveness, benefits, and limitations of various response methods. This report highlights five comparative studies.

The first, Tropical Oil Pollution Investigations in Coastal Systems (TROPICS), established three shallow-water study sites from 1983 to 2015 in Panama to evaluate the impacts of untreated and dispersed oil relative to a control site. The purpose of the TROPICS study was to evaluate the relative health of the ecosystem at each site. In the first 10 years, the plot exposed to dispersed oil had recovered to pre-spill conditions, while the site exposed to undispersed oil still showed negative effects on the mangroves (Renegar et al., 2017b).

The second set of studies involved two CRAs. The CRAs rely on integrated numerical modeling to predict which environmental and human health impacts may arise in various response scenarios.

The first CRA, referred to as CRA-1 to differentiate it from the generic term CRA, was a simulation of a single site with DWH-like oil in the northeastern Gulf of Mexico. It compared oil mass distributions and ecological impact assuming four response options: no response, traditional responses (mechanical, burning, and surface dispersants), mechanical only, and subsea dispersant injection (SSDI) plus traditional responses. For this particular scenario and set of assumptions, SSDI appeared to be at least as effective in reducing impacts on the selected species of concern as all the traditional responses combined (Bock et al., 2018; French-McCay et al., 2018b; Walker et al., 2018a). CRA-2, an extension of CRA-1, explored the sensitivity of the fates to changes in flow rate and blowout location (e.g., distance from shore and water depth). Two sites were considered: a shallower site at 500 m and a deeper site at 1,400 m. Overall, CRA-2 indicates that at 500 m depth, SSDI generally will be less effective in reducing oiling at the surface and at the shore than at 1,400 m depth; at some threshold water depth, SSDI benefits will become negligible (French-McCay and Crowley, 2018).

The third study involves a comparison of VOCs emitted to the atmosphere near the well during a DWH-like blowout using an integrated oil-fates model for the ocean and a numerical model for the atmosphere to compare SSDI with no response. The inputs were similar to those used in CRA-1. The study concludes that SSDI reduces peak VOCs by factors of 100- to 200-fold depending on the winds (Crowley et al., 2018).

The fourth comparison study of note used an alternative integrated fate and effects model to evaluate the effectiveness of SSDI during the DWH relative to no dispersant use. The model was validated using observed concentrations of oil constituents. It was then used to estimate the distribution of oil through the water column with and without SSDI. A DOR of 1:250 was assumed.

In this modeling exercise, dispersant increased the volume of oil retained in the lower water column by 55% and reduced the volume of oil that surfaced resulting in 28% fewer VOCs in the atmosphere (Gros et al., 2017). A follow-up study by Socolofsky and Gros using the same methodologies (see Appendix E) found that a DOR of 1:100 virtually eliminated surfacing of oil for the DWH spill scenario.

The fifth comparison involved a SIMA prepared for an exploration drilling project in offshore Nova Scotia that focused on a source control event (Slaughter et al., 2017). Based on the resources of concern identified in this exercise, dispersant use compared favorably to other response options.

Based on results from these field and modeling studies, surface and subsurface dispersant application represents a useful tool for oil spill response. When used appropriately, dispersants can decrease the amount of oil at the surface, thereby reducing the potential exposure of response personnel to VOCs and decreasing the extent of oiled areas encountered by marine species at the surface. Each response method has a complex suite of advantages and disadvantages, including and not limited to encounter rate, effectiveness, and ecosystem and human health effects that should be considered when developing and executing oil spill response plans. These complex trade-offs are best addressed using NEBA tools such as CERA, SIMA, and CRA.

Recommendation: The NEBA tools (CERA, SIMA, and CRA) should be expanded to consistently address the health of response personnel, community health, and socioeconomic considerations (e.g., beach closures). Furthermore, these tools should be used to gain stakeholder input on local or regional priorities, expand awareness, and gain trust in the decision-making process.

Finding: Experience with historical spills and integrated models consistently indicate that for large spills, dispersants (both SSDI and surface) are a response option that can substantially reduce surface oil.

Finding: The understanding of the impacts of dispersant as a response tool has been greatly advanced by laboratory experiments and modeling, but these efforts are often limited by their inability to capture the complexity or scale found in the field. Important issues that are best answered in a field study or future spill (spill of opportunity) cover a broad spectrum of topics, including validation of integrated models and their sub-models, especially scaling of droplet size; better understanding of health impacts on response workers (unintentional releases only); validation of response decision-making approaches; and discovery of previously unknown linkages in complex ecosystems affected by oil.

Recommendation: Efforts to take detailed scientific measurements during future spills (spills of opportunity) and/or to conduct dedicated field experiments should be strongly encouraged. In the case of a spill of opportunity, preplanning and pre-deployment as well as focusing on the priorities for such observations are essential to avoid delays in the start of taking these measurements. Given its long-term funding and mandate, the National Academies Gulf Research Program,[8] or a foundation with similar long-term funding, would be in an ideal position to work with the Interagency Coordinating Committee on Oil Pollution Research to coordinate a field experiment or scientific efforts for deployment in a spill of opportunity.

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[8] As a result of settlements from the DWH spill, $500 million were designated to the development and 30-year endowment of the National Academies Gulf Research Program, whose mission is "catalyzing advances in science, practice, and capacity to generate long-term benefits for the Gulf of Mexico region and the Nation." In furtherance of its mission, the National Academies Gulf Research Program funds grants, fellowships, and activities.

CHAPTER 1

INTRODUCTION

Each oil spill in the marine environment is unique and challenges responders, who must balance decisions to account for immediate and potential long-term human health, socioeconomic, and environmental impacts. Oil spills at sea may result from a variety of incidents, including an oil well blowout, a vessel collision or grounding, or a leaking pipeline. Additionally, the location, time of year, duration of the spill, water depth, environmental conditions, affected biomes, potential community impact, and available resources may also vary significantly.

The unique context of each spill requires that responders have access to a variety of response options that can be applied based on the specific conditions of the spill. Having a variety of response options available in the “tool kit” provides responders with alternatives in the face of operational limitations. Marine oil spill response methods include mechanical recovery of oil through skimmers and booms, in situ burning of oil, monitored natural attenuation of oil, and dispersion of oil by dispersants. Booms and berms may also be employed at the shoreline to minimize the impact of oil on shoreward resources, or to divert oil from a more sensitive area of shoreline to another, less sensitive area. Natural attenuation and biodegradation processes can substantially contribute to a reduction in the volume of oil from a spill.

Each response method has advantages and disadvantages. For example, the containment and mechanical recovery of oil has the advantage of removing the oil from the environment, but it is a very slow process that is limited by weather. In situ burning has the potential to remove significant quantities of oil from the sea, but ignition generally requires that the oil slick be reasonably fresh and sufficiently thick. Dispersants have the advantage of being able to treat large areas/volumes of oil, but they rely on other processes, such as biodegradation by microbes, to remove the oil from the environment. Several other factors also play a role in determining which response techniques will be most effective on their own or in combination with other approaches. It is often a combination of tools and adaptability based on circumstances that affords the optimal response outcomes. This report focuses on the factors that contribute to the decision as to whether to use dispersants as a response tool for any given marine oil spill. In oil spill response decision making, it is important to understand specific scenarios where a net benefit may be achieved by using a particular tool. With regard to dispersants, the primary objective is to prevent or reduce the formation or thickness of surface oil slicks. Dispersants accomplish this by reducing the oil-water interfacial tension, and, with sufficient mixing energy, increasing the formation of small droplets that become or remain entrained in the water column with minimal recoalescence and slow resurfacing.

Modern dispersant formulations (see Box 1.1) contain one or more surface active agents (surfactants) that align at the oil-water interface allowing for wave action or other turbulence to cause the formation of droplets on the order of 70 microns (μm) or less. The dispersed droplets retain the initial buoyancy of the bulk oil itself (i.e., they remain less dense than the surrounding water in most cases) but rise more slowly through the water column by virtue of physical processes associated with their small size. Conceptually, a key potential advantage of these oil microdroplets[1] is that the increased surface area-to-volume ratio provides more substrate with which microorganisms may interact, thus enhancing oil biodegradation, assuming no other limitations imposed by the environment (see Chapter 2). These smaller droplets are susceptible to colonization by naturally occurring oil-degrading microorganisms and may potentially biodegrade more quickly compared to oil in a floating slick, emulsified oil, or oil stranded on the shoreline. Similarly, the increase in surface area may promote greater dissolution.

Dispersant use also offers the opportunity to respond rapidly to large-scale, offshore marine surface or subsurface spills, especially with the recent advent of subsea dispersant injection (SSDI) capabilities and the use of jet aircraft delivery platforms. These advances in technology expand the operational window of opportunity, which was formerly more limited by hours of daylight, weather conditions, distance, and remoteness of a spill site (Chopra and Coolbaugh, 2016). These advances in dispersant application technology provide the opportunity to respond to a spill before oil weathers to the point where most other response options become less effective. Furthermore, subsurface application of dispersant may reduce responder exposure to volatile organic compounds (VOCs) known to be hazardous to human health.

When reading this report, it is important to consider the circumstances for which dispersants would be considered as a potential response option. For example, for small spills or in particular sea state conditions, it may not be logistically feasible to mount a dispersant operation. Similarly,

BOX 1.1
Dispersant Components

Modern dispersants consist of a mixture of surface active agents (surfactants) dissolved in a solvent or mixture of solvents. In standardized tests, eight dispersants listed on the U.S. Environmental Protection Agency National Contingency Plan Product Schedule were generally classified as slightly toxic to practically nontoxic based on acute toxicity to two species, *Menida beryllina* and *Mysidopsis bahia* (Hemmer et al., 2011). Dispersants can be applied through various methods depending on the type of delivery platforms available. (See NRC [2005] for a more complete discussion.) Ingredients often include:

- Non-ionic surfactant—typically sorbitan oleate and polyethoxylated derivatives
- Anionic surfactant—primarily dioctyl sodium sulfosuccinate
- Hydrocarbon solvents—typically hydrotreated light distillates
- Other solvent—typically a glycol ether derivative

NOTE: Nonylphenol ethoxylates are present in some commercial formulations, but these are generally less acceptable to regulatory authorities because of the concern that they may break down to a nonylphenol, which may pose reproductive health and chronic aquatic toxicity concerns.

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[1] The committee recognizes that the term "microdroplets" is loosely defined, but in this report the term typically means droplets that are approximately 70 microns or less. A notable exception is in Chapter 3.

in the United States, preauthorization zones for dispersant use are generally limited to areas greater than 3 nautical miles from shore and in depths greater than 10 m. In other parts of the world, these zones may differ. Also, although a few freshwater dispersant products are available on the market, they are not currently approved for use in freshwater in the United States. Therefore, the committee interpreted the Statement of Task as limited to marine oil spill scenarios in which dispersants would be considered a potential response option.

HISTORICAL CONTEXT FOR DISPERSANT USE

One of the first major incidents where chemicals were used to disperse oil in the marine environment was on March 18, 1967, when the SS *Torrey Canyon* ran aground off the southwest coast of the United Kingdom. In that case, however, the chemicals used to respond to the *Torrey Canyon* were not specifically formulated for oil spill response and were not designed to minimize environmental damage. In fact, the products used during that response consisted of chemical degreasers with high levels of aromatic compounds that could be harmful to aquatic organisms but were very effective at transferring floating slicks into the water column. Since that time, a number of products have been developed that are much less toxic and are more effective on a wide range of oils.

Just over two decades later, in 1989, the T/V *Exxon Valdez* struck a reef in Prince William Sound, Alaska. One result of the ensuing oil spill was passage of the Oil Pollution Act of 1990 (101st Congress H.R. 1465, 1990), which had a tremendous impact on positioning the maritime community to better prepare for marine oil spill response. The act mandated vessel and facility response plans with specific minimum equipment and personnel capabilities for oil containment and recovery. The act also called for national and regional response teams to develop guidelines for spill preparedness and response strategies. This resulted in some regions in the United States identifying zones where dispersants and in situ burning are "pre-authorized" for use.

The U.S. Coast Guard (USCG) published a Final Rule on September 30, 2009 (74 FR 45003), titled *Vessel and Facility Response Plans for Oil 2003 Removal Equipment Requirements and Alternative Technology Revisions.* The Final Rule updated the requirements for spill response equipment associated with vessel response plans and marine transportation-related facility response plans. It provided additional requirements for new response technologies and modified response methods and procedures for marine and aquatic spills within the jurisdiction of the United States. This Final Rule clarified requirements for response capabilities, including effective daily application capacity for dispersants, using an Office of Natural Resources Revenue, the National Oceanic and Atmospheric Administration (NOAA) dispersant planning calculator known as Dispersant Mission Planner 2.

Since the *Torrey Canyon*, dispersants have been applied in the United States approximately 20 times (Bejarano, 2018) and are routinely used internationally, including during the 1979 Ixtoc I spill and the 2009 Montara spill (described below).

The Ixtoc I spill off Campeche, Mexico, was a shallow-water (54 m water depth) marine blowout that persisted for more than 9 months (Soto et al., 2014). The spill released about 3.3 million barrels (bbl) of crude oil and was the first spill in which large quantities (approximately 9,000 metric tons) of dispersants (mostly Corexit® products) were used via surface application (Jernelöv and Lindén, 1981; Linton and Koons, 1983).

In Western Australia, seven different dispersants (totaling 48,000 gallons) were applied at the surface during the Montara wellhead blowout in 2009. This spill involved the continuous release of approximately 30,000 bbl of a waxy crude oil into the Timor Sea over 10 weeks. Although this spill was a subsea blowout, the platform remained intact and the oil from this spill was released at the surface. The extent of dispersant effectiveness and overall potential impacts from this spill are still being litigated within the Australian federal courts.

A recent use of an unprecedented amount of dispersants in a major marine incident came as a result of the *Deepwater Horizon* (DWH) oil spill (also referred to as the Macondo oil spill), which occurred in the Gulf of Mexico in 2010. The DWH spill started as a well blowout and explosion from a mobile offshore drilling unit, followed by the collapse and sinking of the platform to the seafloor, resulting in a continuous release of oil and gas from the subsea well for 87 days (National Commission, 2011). During the DWH spill, the use of dispersants on the surface was preauthorized under the Gulf Coast Area Contingency Plan; and, with the oil release taking place more than 40 miles offshore, responders quickly commenced the application of dispersants on the surface.

This was followed by an unprecedented subsea injection at the wellhead, which required a difficult decision, because there was an "absence of information on the effects of dispersants in the deepwater environment" (National Commission, 2011). In weighing the trade-off decision, responders reasoned that subsea injection might reduce the overall volume of dispersants needed; worker safety would be improved on the surface due to less VOCs in the vicinity of the ongoing well control work; and less oil would reach the sensitive and fragile Gulf Coast shoreline (National Commission, 2011). The National Commission's report noted that the decision for subsea injection was appropriate at the time based on all the factors considered.

Since the 2010 DWH spill response, the petroleum industry has invested significantly in the purchase of the most studied modern products (Dasic Slickgone NS, Finasol® OSR 52, Corexit® EC9500A) and their placement in strategic global locations to facilitate rapid response in an event where dispersants represent a viable response option (see Figure 1.1).

While a variety of dispersant products are available globally, regulatory considerations are key to their potential use. Figure 1.2 lists the countries where dispersants were considered as either a primary or a secondary response option as of 2013. The list of countries is likely to change over time.

FIGURE 1.1 Example of Global Dispersant Stockpile. SOURCE: Oil Spill Response Limited.

FIGURE 1.2 Countries that allowed dispersants to be considered as a response tool during an oil spill as of 2013. SOURCE: Figure based on International Tanker Owners Pollution Federation information and used with permission from The Clearing, Washington, DC.

TOOLS TO EVALUATE RESPONSE TRADE-OFFS AND STRATEGIES

There are many perspectives and perceptions surrounding the impact that dispersants and dispersed oil have on the environment and on human health. The decision to use dispersants to prevent oil from reaching the surface or to transfer surface oil into the water column is often seen as a difficult decision which involves consideration and evaluation of trade-offs with other response options.

Since the 1970s, approaches to environmental trade-off analysis for spill response planning have evolved. These approaches, collectively known as Net Environmental Benefit Analysis (NEBA), help decision makers select the most appropriate response option(s) to minimize the net impacts of oil spills on the environment. The U.S. Environmental Protection Agency (EPA) describes NEBA as a method for identifying and comparing the environmental benefits associated with alternative management options in spill response. As described in IPIECA-IOGP (2015) and ASTM (2019), NEBA does not include human health, but its scope varies among different countries. In other countries, the process may include an analysis of net benefits to people, such as the consideration of socioeconomic sensitivities and costs (IPIECA-IOGP, 2015).

For planning purposes, a NEBA needs to consider a broad range of geographic areas, ecological habitats, environmental, oceanographic, and climatological information because it is unclear exactly when or where an actual oil spill might occur. Similarly, an effective NEBA accounts for the fact that an ongoing spill event is highly unpredictable, and the range of ecological receptors potentially affected can be enormous. This requires that NEBA processes be highly flexible and use a comparative risk process that can be adapted in "real-time" to align with changing field conditions.

Three tools that support the NEBA conceptual approach include:

- Consensus Ecological Risk Assessment (CERA)
- Spill Impact Mitigation Assessment (SIMA)
- Comparative Risk Assessment (CRA)

Each process involves a structured approach used by the response community and stakeholders to compare the impact mitigation potential of candidate response options. Additionally, these three NEBA tools all consider realistic response measures and identify the best overall set of actions that will promote the most rapid recovery. The three tools can each be adapted to fit various regulatory and environmental contexts. Distinct differences in these approaches exist in terms of the degree and timing of stakeholder engagement as well as the type and complexity of environmental analysis, such as the extent to which numerical models support the process. A more comprehensive discussion of the NEBA methodology is provided in Chapter 6.

RATIONALE FOR CURRENT STUDY

As mentioned previously, the use of dispersants is not a novel approach to oil spill response. To that point, the National Research Council (NRC) released two previous reports, in 1989 and 2005, that focused on the use of dispersants at sea in response to a spill. The NRC report titled *Using Oil Spill Dispersants on the Sea* (1989) was commissioned to "review the state of knowledge in toxicity, effectiveness of application techniques, and effectiveness of commercially available dispersants" (NRC, 1989). At that time, much research on dispersant use had been conducted by industry in the United States and abroad, and the report assessed the state of knowledge and practice about the use of dispersants. That report concluded that the use of dispersants can be an effective spill response and control method, especially to minimize environmental damage caused by the presence of surface slicks, but the method for applying dispersants is a critical factor.

Shortly after the 1989 NRC report was completed, the Oil Pollution Act of 1990 was adopted. In the late 1990s, a series of workshops conducted by the USCG further examined the trade-offs associated with multiple response options, including dispersants. In 2003, a multiyear rulemaking process commenced to enhance the oil spill contingency planning regulations. This prompted the former Minerals Management Service (now the Bureau of Ocean Energy Management and the Bureau of Safety and Environmental Enforcement), NOAA, the USCG, and the American Petroleum Institute to request that the National Academies form a committee to examine the state of science on dispersants. The committee was tasked with considering the adequacy of existing information and ongoing research regarding the efficacy and effects of dispersants as an oil spill response technique in the United States (NRC, 2005). That request resulted in the NRC 2005 report titled *Oil Spill Dispersants: Efficacy and Effects.*

This current report builds on the two previous reports by incorporating the tremendous amount of subsequent research on dispersants. The DWH spill and the resulting funds from litigation and penalties (see Figure 1.3) have led to a rapid increase in the volume of science and literature surrounding oil spill response and dispersant use in particular.

The use of SSDI in the DWH spill raised new questions and challenges focused on the fate and effects of dispersant and dispersed oil, especially in the deep ocean. As the studies prompted by this spill are in various stages of completion, an understanding of the impacts of dispersant use as well as the potential limitations and benefits—particularly in scenarios similar to the DWH—is continuing to develop.

In light of this expanded body of knowledge since the previous National Academies publications on dispersants, this report highlights and synthesizes new information on the topic. The committee recognizes that this is an area of ongoing research, and it strives to provide as much complete and current information as possible to inform decision makers and other stakeholders. While most literature cited in this report has been released since the 2005 report, this was not a requisite criterion, and, where appropriate, the committee does cite earlier literature as well. Similarly, the committee acknowledges that much of the recent literature focuses on the DWH oil spill; however, this report is not intended to be a retrospective evaluation of that event. Instead, the committee intends for this report to be forward looking and applicable to future offshore marine spill scenarios. Where possible, the committee relied on peer-reviewed publications; however, the committee also recognized the value of other sources of information, including and not limited to industry reports, conference proceedings, and guidance documents.

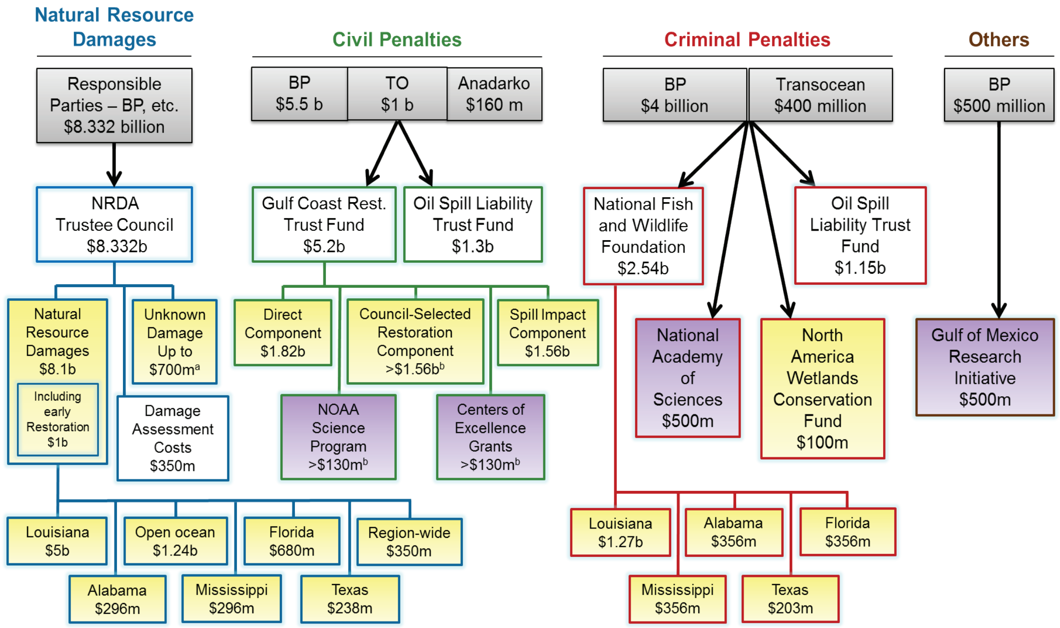

FIGURE 1.3 The *Deepwater Horizon* oil spill resulted in both criminal and civil penalties as well as other fines and expenditures. This figure depicts how those fines were distributed and represents a significant influx of resources for research in the field of oil spill response. NOTES: According to NRC, 2017: "[a]Unknown NRDA damage includes $232 million plus interest on the $8.1b payment. [b]The Comprehensive Plan Component is supplemented by 50% of the interest on RESTORE funds, and the remaining interest is split between the NOAA Science Program and the Centers of Excellence grants." SOURCE: NRC, 2017.

STATEMENT OF TASK AND REPORT ORGANIZATION

Addressing the Statement of Task (see Box 1.2) requires consideration of the objectives of an oil spill response, the factors that contribute to response decision making, the trade-offs associated with the use of dispersants, and the processes available for assessing these trade-offs.

Chapter 2 focuses on the first task by considering processes associated with the fate and transport of oil, dispersed oil, and dispersants in the marine environment. Chapter 3 addresses the second task and discusses aquatic toxicity and ecological consequences of exposure to oil, dispersed oil, and dispersants. Next, Chapter 4 answers the fourth task by exploring the potential human health concerns associated with oil spill response and the use of dispersants, with a particular focus on occupational health, community psychosocial impact, and seafood safety. In Chapter 5, the committee partially responds to the sixth task and reviews the tools available and the information necessary for evaluating risk and making decisions regarding the use of dispersants and other response options. Drawing from the previous chapters, Chapter 6 compares the benefits and limitations of using dispersants to other response methods, as called for in the third task. Finally, and in accordance with the fifth task, the committee also considers the research protocols and standards that would increase the applicability and comparability of field and laboratory research in Chapter 7. Throughout the report, the committee further responds to the sixth task by identifying information necessary for decision making and additional research and modeling needs.[2]

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[2] Since the release of the prepublication version, the text was edited for clarity and references have been checked and modified as necessary.

BOX 1.2
Statement of Task

This study will assess the effects and efficacy of dispersants as an oil spill response tool through review and evaluation of domestic and international research reports and results, including both field and laboratory studies. The study will evaluate trade-offs associated with dispersant use, in part through use or review of net environmental benefit analyses conducted for past oil spills.

This evaluation will include comparison of chemically dispersed oil with the fate and effects of *untreated* oil. As part of this study, the committee will review research on the use of dispersants during actual spills, both for surface and subsurface applications (e.g., the 2009 Montara oil spill off the Australian coast and the 2010 *Deepwater Horizon* oil spill in the Gulf of Mexico) to assess the net benefit of dispersant use in these cases. Specifically, the study will:

1. Assess the state of our knowledge about dispersant effectiveness (including comparisons across a range of dispersant formulations) and the fate, including short- and long-term fate, of untreated oil (no chemical dispersant applied), chemical dispersants, and chemically dispersed oil and the influence of dispersants on deposition (including marine snow), biodegradation, and/or transport of oil;
2. Evaluate and summarize research on the acute and chronic (sublethal) toxicity of chemical dispersant formulations of comparable efficacy, chemically dispersed oil, and untreated oil at realistic environmental exposure levels. This will include characterization of the relative risks to wildlife health of untreated oil and chemically dispersed oil, taking into consideration exposure to volatile compounds, ingestion, and absorption of naturally versus chemically dispersed droplets;
3. Compare the benefits and limitations of dispersant application to the use of other clean-up methods (e.g., no-action, mechanical recovery, burning, and chemical herders in combination with burning);
4. Compare the relative human health risks for the use of dispersants with the use of other clean-up methods (exposure of response personnel and residents in Gulf coastal communities to oil and dispersants, and contamination of seafood);
5. Identify the research protocols and standards that would: (i) increase the applicability of lab-based measurements to the field, and (ii) improve the comparability of research findings from different laboratories; and
6. Assess the adequacy of the existing information to support risk-based decision making or net environmental benefit analysis of response options under a variety of spill scenarios and recommend a "roadmap" of research and modeling to address identified information gaps.

CHAPTER 2

FATE AND TRANSPORT

INTRODUCTION

Upon discharge to the environment, dispersants and oil are subject to a host of processes that act to transport and transform that discharge. Because such processes act in concert, the phrase "fate and transport" is commonly used to describe the collective action of these processes. The limited literature available on the fate and transport of dispersant components is briefly summarized at the start of this chapter. The remainder of this chapter examines how the use of dispersants as an oil spill countermeasure changes the characteristics of oil and the relative importance of physical, chemical, and biological processes that impact oil upon discharge to the environment. As an update from the 2005 National Research Council (NRC) report, this chapter includes a combination of foundational information and new knowledge gained since the publication of the previous report. While the primary focus is on the capacity of dispersants to alter oil's fate and transport, the chapter also considers feedbacks between processes with a leaning toward the subsurface, owing to studies that followed the *Deepwater Horizon* (DWH) oil spill (also known as the Macondo spill).

FATE AND TRANSPORT OF DISPERSANT COMPONENTS

The mixture of solvents and nonionic and anionic surfactants that comprise typical commercial dispersants (Place et al., 2010) contains compounds with different physicochemical properties and therefore potential fates in the environment. Once introduced to open ocean waters, dispersant mixtures will be quickly diluted (Lee et al., 2013a) and subjected to degradation processes, including biodegradation and photodegredation.

Laboratory-based experiments have shown that components of the dispersant mixture are biodegradable on the order of days. This biodegradability includes the petroleum distillates (Bælum et al., 2012) as well as the surfactant compounds dioctyl sodium sulfosuccinate (DOSS), Tween 80, and Tween 85 (Brakstad et al., 2018b; Campo et al., 2013; Garcia et al., 2009). Direct sunlight and indirect photolysis via reaction with a hydroxyl radical have also been shown to degrade the surfactant components of dispersants on the order of hours. These studies include the photodegradation of DOSS, 2-butoxyethanol, dipropylene glycol butyl ether, and propylene glycol (Glover et al., 2014; Kover et al., 2014). These lab-based studies indicate that dispersant mixtures, when released into the environment, are generally biodegraded and/or photodegraded on the order of hours to days. In the few field studies conducted, the effects of dilution on dispersant fate and transport have also been observed. Measured concentrations of dispersants after surface applications reached a maximum of 5-13 parts per million (ppm) at 1-0.6 m depth (Bocard et al., 1984; Lewis and Aurand, 1997). Prior research suggests that concentrations should decrease to < 1 ppm within minutes to hours (Lewis and Aurand, 1997).

Research examining the long-term fate of dispersant mixtures in the environment indicates that DOSS is not always completely degraded. Studies have shown that DOSS persisted for up to 4 years following the DWH spill in oil-sand patties collected from beaches along the Gulf of Mexico (McDaniel et al., 2015; White et al., 2014) and in marine sediment material (Perkins et al., 2017). DOSS measured in samples collected from beaches is thought to originate from dispersant applications at the surface, while DOSS in the deep sea could originate from both surface applications and subsea dispersant injection (SSDI). In the aforementioned scenarios, however, the concentrations of DOSS observed were extremely low (~1-260 ng/g or parts per billion [ppb]) indicating that dissolution, biodegradation, and photodegradation likely acted on the bulk of dispersant released in response to the DWH spill.

CHARACTERIZATION OF OIL CHEMISTRY

The chemical composition of an oil dictates its physical properties, which in turn dictate the initial physical interactions of oil with applied dispersant. The chemical composition of an oil further dictates the long-term behavior of dispersed oil through processes such as evaporation, dissolution, biodegradation, aggregation, and adhesion. This section introduces oil chemistry, especially as it relates to spill response and dispersant application.

Throughout this report the term “oil” is used as a general term referring to complex crude and refined chemical mixtures of hydrophobic compounds derived from geological sources. The term “petroleum” is used interchangeably with oil for the purpose of this report, and both terms are used with various modifiers for added specificity. The chemical composition of an oil typically includes thousands of different compounds (Frysinger et al., 2003; Hsu et al., 2011) and can vary significantly between geological sources based on the organic source material, geologic setting, thermal history, occurrence of subsurface biodegradation, and physical fractionation processes (Hunt, 1996; Peters et al., 2005). Following extraction, an oil may be further altered by various industrial actions, among them simple phase separations at the site of production; refining process, including various modes of distillation, condensation, desulfurization, and cracking; and blending of crude or refined materials for transport or sale. The combination of source-specific compositional variability with complex and variable industrial processing leads to a complex terminology for oil spill responders that includes functional classification of industrial products, functional descriptions of chemical composition, specific methodologies used to derive chemical composition, and multiuse terminology. Because any of these products can spill to the environment, nuances of the terminology are relevant to the issue of dispersant application.

Crude petroleum is typically described by bulk physical or chemical properties relevant to transport, refining, or potential profitability. Common descriptors include categorization of the American Petroleum Institute (API) Gravity (a measure of density) as light, medium, or heavy, and categorization of the sulfur content as sweet or sour. Other common descriptors define the method by which the petroleum was extracted—conventional versus nonconventional—as well as select physical properties relevant to its handling, such as viscosity, vapor pressure, and tendency to solidify as wax. Following processing or refining of crude oil the product is referred to explicitly, with an implicit understanding of the associated properties and behavior. Examples include gasoline, jet fuel, avgas, diesel fuel, heavy fuel oil, natural gas, gas condensate, light naphtha, and kerosene. Such products typically contain a subset of compounds found in crude petroleum, and their chemical composition is thus more readily defined. Subsea well blowouts such as occurred in the DWH, the 1969 Santa Barbara, and the Ixtoc I oil spills occur at seafloor temperature and pressure conditions and involve the unprocessed reservoir fluids that may include natural gas, reservoir water, carbon dioxide, and crude oil. More so than for surface spills, the circumstance of such blowouts—particularly the gas composition (see Box 2.1)—necessitates a situational understanding of the basic chemical properties of the discharge at in situ conditions, relevant to the consideration of response options, including SSDI.

In the absence of published studies on the compositional variability of discharge from a well blowout, the committee turned to reservoir geochemistry (Hunt, 1996) to assess potential heterogeneity in discharged fluids. While large reservoirs are relatively homogenous, smaller or complex reservoirs tend to exhibit greater heterogeneity relevant to a blowout scenario. For example, the pressure change in a small reservoir over the course of a blowout could be substantial, and if the reservoir pressure passes near the bubble point of the oil it will result in a change in the gas-to-oil ratio (GOR), which in turn can result in a migration of the lighter oil constituents from the oil to the gas. In other words, not only will the GOR change but both the oil and gas components will become heavier. In complex reservoirs—which may be faulted, be partially biodegraded, or have non-horizontal strata—the oil may have fractionated during its geological life such that as a blowout progresses, different fractions may emerge. This tendency will be enhanced for smaller reservoirs. The relative proportions of gas, water, and oil typically change over the production life of a well, with an expectation that these proportions could vary for a blowout scenario.

Comprehensive and quantitative chemical inventories exist for some refined petroleum products, whereas molecular complexity has challenged such characterization for crude oil. As a result, chemical descriptions of crude oil rely on distinctions between molecular composition at the level of functional moieties, molecular weight distribution, solubility behavior, volatility distribution (e.g., volatile organic compounds [VOCs], semi-volatile organic compounds [SVOCs], and intermediate-volatility organic compounds [IVOCs]), physical transformations (such as wax formation, as occurred extensively during the Montara oil spill), abundance of minor elements, and the relative abundance of readily quantified compounds. Various methods have been developed to quantify oil's chemical composition, though no single method is able to provide a complete chemical inventory.

According to various dispersant application guidelines, many liquid petroleum products have too high a viscosity or pour point to be effective targets for chemical dispersion. Key compositional determinants of physical behavior include the molecular weight distribution of hydrocarbons, the abundance of other elements (e.g., N, S, and O), and the relative abundance of saturates, aromatics, resins, and asphaltenes. As a general rule, a disproportionate abundance of high molecular weight hydrocarbons (exemplified by the Montara oil spill), high relative concentrations of resins or asphaltenes (exemplified by the 1969 Santa Barbara oil spill), and high abundances of other elements are associated with high viscosity and high pour point. In cases of dispersant application, it is important not only to know the initial properties of the discharged oil but also to know sufficient compositional details in order to predict how the oil might change as it weathers. Such compositional information is useful for predicting fate and transport processes.

Oil fate and transport mechanisms are governed by the laws of physics and chemistry. In practice, the application of these laws is strongly modulated by the chemical composition of the oil, the spill environment, human intervention, biological processes, and time (Daling et al., 1997). This chapter is arranged to follow the major processes that act on oil in the environment, which provide the context for subsequent chapters.

The application of dispersant can alter the relative importance of different fate and transport processes as outlined in Figure 2.1, with the intention of enhancing processes such as dispersion, oil droplet formation, dissolution, vertical and horizontal mixing, and biodegradation (see Figure 2.2a). Aerosolization and aggregate formation may also be enhanced by chemical dispersants (see Figure 2.2a). The efficacy of dispersants can be hindered directly or indirectly by processes such as evaporation, emulsification, and photochemical oxidation (see Figure 2.2b). This chapter focuses on processes that inform or influence the effects of chemical dispersant use, with a brief overview of other processes.

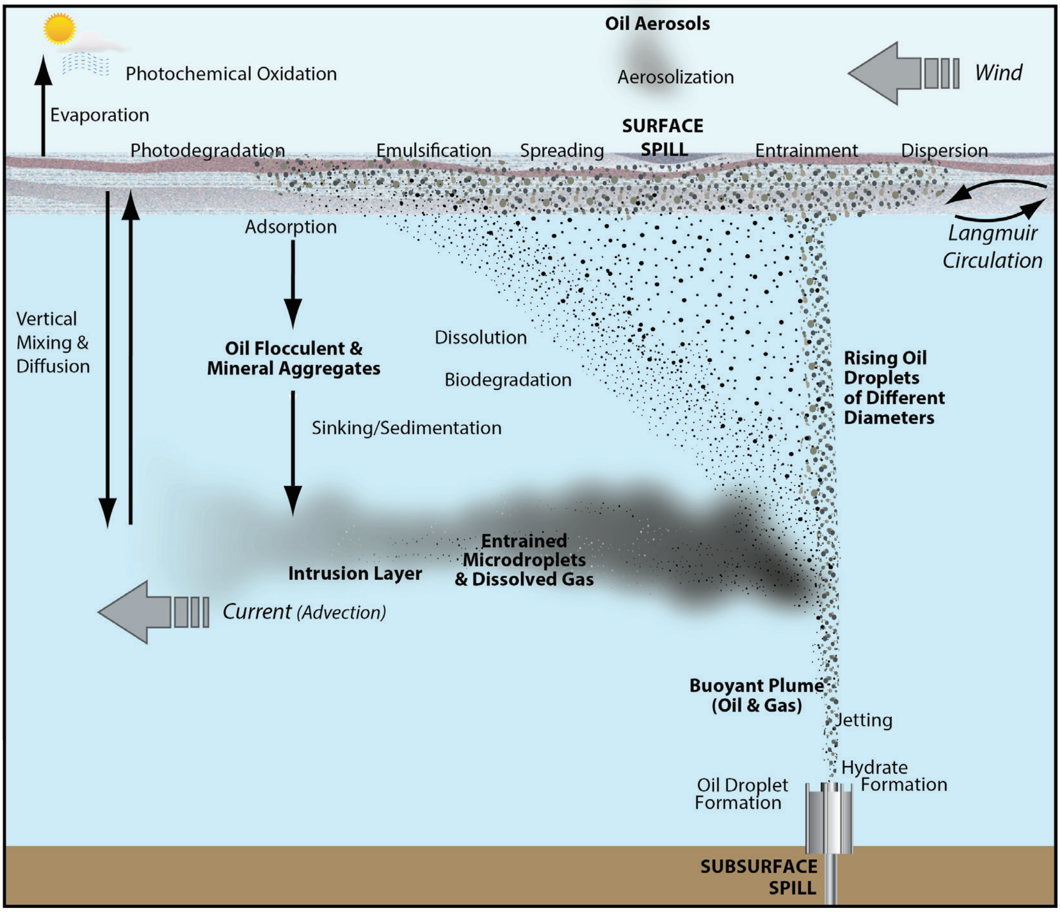

FIGURE 2.1 Summary of the important components (bold font) of an oil spill and the processes (normal font) that affect them. Dispersants may exert an influence on all processes shown except for jetting, wind, current, and Langmuir circulation. Surface gravity waves are not explicitly shown for the sake of clarity. SOURCE: Modified from Hazen et al., 2016.

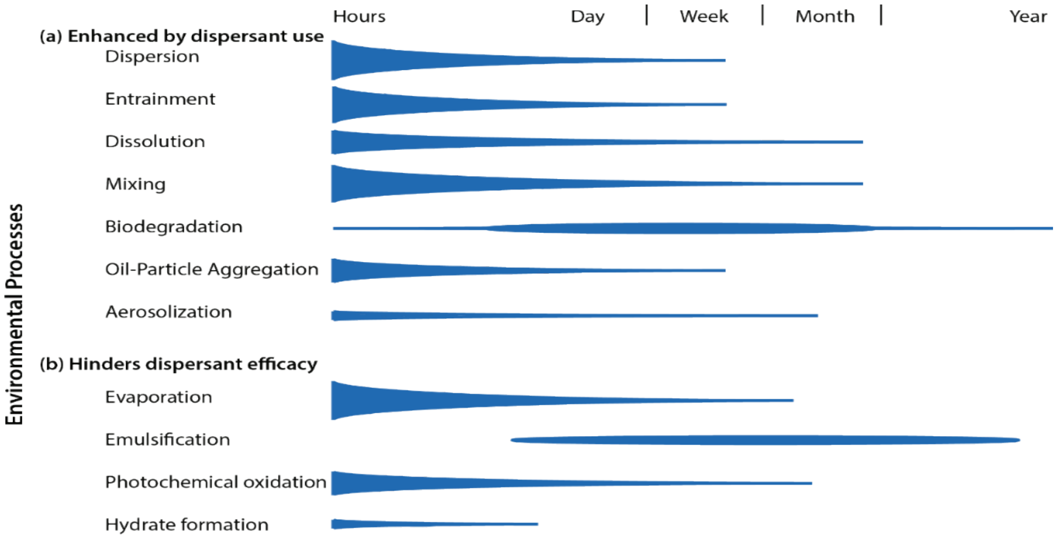

FIGURE 2.2 Time scales of environmental processes affecting oil spills that (a) are enhanced by dispersant use or (b) may hinder the efficacy of dispersants. SOURCE: Modified from Ward et al., 2018b (available at https://pubs.acs.org/doi/10.1021/acs.est.7b05948; further permissions related to the material excerpted from this article should be directed to ACS Publications).

THE EFFECT OF NATURAL GAS IN BLOWOUTS

The occurrence of natural gas is a defining feature of a blowout scenario, and it affects myriad processes, as described in this section and in Box 2.1. Natural gas refers to the low molecular weight hydrocarbons that maintain a gaseous state at atmospheric pressure and temperature, typically comprising methane as the bulk constituent with variable concentrations of ethane, propane, butanes, and pentanes. These hydrocarbons are produced through the same geologic processes that produce higher molecular weight petroleum hydrocarbons, though natural gas occurrence is variable among oil reservoirs because of reservoir source material and thermal history, phase separation, and microbiological activity. Natural gas is typically separated from crude oil following extraction and prior to transport; as a result, it is a nonissue for many oil spills. The major exception is for well blowouts. Natural gas discharged from the seafloor during a blowout can be dissolved in oil (referred to as live oil), or it can occur as a separate phase with consequences on the fate and transport of the oil and, therefore, on the response efforts. Box 2.1 outlines several impacts that the presence of gas had on the response operations during the DWH spill: hydrate formation, estimation of flow rate, dispersant-to-oil ratio (DOR), and mass balance calculations. The occurrence of natural gas can impact oil droplet formation and transport in various ways, relevant to SSDI. The occurrence of the gas phase at the point of discharge played an important role in droplet formation and rise velocity, as identified in various models: for example, SINTEF's model[1]; VDROP-J (Zhao et al., 2014a); and RPS ASA's model.[2] These models *assume* that the gas and oil are co-flowing, in which case the oil is effectively squeezed through a smaller cross-section with commensurate increase to its velocity and Weber number, predictably decreasing droplet size

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[1] For the purpose of clarity, in this discussion, the committee uses "SINTEF's model" here and henceforth to refer to the model initially developed by Johansen et al. (2013) and subsequent modifications of that model.

[2] For the purpose of clarity, in this discussion, the committee uses "RPS ASA's model" here and henceforth to refer to the model initially developed by Li et al. (2017c) and subsequent modifications of that model.

BOX 2.1
The Implications of Natural Gas on DWH Spill Response Efforts

This box considers lessons learned about natural gas discharge in the context of DWH, including the relation to SSDI.

The temperature and pressure conditions of the Macondo Reservoir that sourced the DWH discharge were such that natural gas occurred homogenously with other petroleum hydrocarbons in a single supercritical state (Oldenburg et al., 2012). The initial blowout of the Macondo well that triggered the explosion on the DWH drilling unit was caused by the exsolution, expansion, and atmospheric discharge of natural gas that had passed through a failed concrete seal (National Commission, 2011). The discharge of this gas at great depth was a major defining feature of the DWH spill.

According to Reddy et al. (2012), the quantity of natural gas released from the Macondo well was 1.7×10^{11} grams, representing ~24% of total discharge. The natural gas comprised (by mass) 61.6% methane, 11.5% ethane, 10.7% propane, 8.9% butanes, and 7.3% pentanes. However, this value is based on direct plume capture and is lower than other estimates by as much as a factor of four (Joye et al., 2011).

The occurrence of abundant natural gas in the Macondo discharge affected the spill and response in several ways. One of the early response efforts to intercept and collect discharge involved using a cofferdam to collect oil. However, upon emplacement, the natural gas present in the discharge mixed with ambient seawater, cooled, and formed gas hydrate; this sequence of events clogged the cofferdam, leading to its abandonment. Subsequent intervention efforts, including the top hat and the choke line, were designed and implemented to prevent the entrainment of water that would lead to hydrate formation and clogging. Because natural gas was captured in proportion to oil from these interventions, surface response efforts included gas handling as depicted by the flaring shown in Figure A.

Additionally, the abundance of natural gas complicated the oil flow rate calculation (McNutt et al., 2012). The rapid exsolution of natural gas from the liquid phase at or prior to the point of environmental discharge introduced uncertainty in the estimation of liquid oil flow rate. This ultimately impacted the dispersant-to-oil ratio used for injection and complicated the mass balance calculations.

FIGURE A Flaring of natural gas during the DWH response. Photo credit: David L. Valentine.

(Brandvik et al., 2019b). However, interactions between the two phases are also known to generate a variety of secondary flows, including churn flow (Boufadel et al., 2018b), which complicates assessment of flow rate and droplet size distribution. Degassing of oil in the rising plume has also been hypothesized to accelerate rise velocity for dual-phase droplets (Pesch et al., 2018).

Natural gas may also impact an SSDI scenario through physical and chemical interaction with dispersants, and through two or more possible mechanisms of action. A first point of uncertainty is the impact of a gas phase on the microscale distribution of surfactants because surfactants will migrate to oil–water, gas–water, and gas–oil interfaces, with impacts for efficacy of oil dispersion. A second point of uncertainty is the formation of gas hydrate rinds at the bubble interface and their potential to impact dispersant efficacy. The DWH discharge and the intrusion layers occurred within the gas hydrate stability field, and while direct evidence of water column hydrate formation presented by Joye et al. (2011) is weak, microscale formation remains a possibility.

Upon discharge to the environment from the Macondo well natural gas would have existed in three key forms: gas, liquid, and aqueous dissolved. The gas phase observed exiting the Macondo well is assumed to be primarily methane, whereas ethane, propane, butanes, and pentanes were presumably condensed to the liquid phase at these conditions and occurred homogenously with the higher molecular weight petroleum hydrocarbons. Because of their high solubility and partial pressure, dissolution to the aqueous phase commenced upon aqueous exposure. Observations from June 2010, during a period of regular SSDI, indicate extensive natural gas dissolution to the intrusion layers (Kessler et al., 2011a; Valentine et al., 2010) and minimal atmospheric release (Ryerson, 2010, 2012; Yvon-Lewis, 2011). Limited observations from May 2010, prior to regular SSDI, also indicate extensive dissolution of natural gas to the deep intrusion layers (Joye et al., 2011a).

The natural gas dissolved in the deep-sea intrusion layers (see Figure 2.3) became bioavailable to microbial populations that use these compounds as sources of energy and cellular carbon (Dubinsky et al., 2013; Redmond and Valentine, 2012; Rivers et al., 2013). Several works address the sequence and rate at which microbial populations responded to the input of natural gas and other soluble compounds. Measurements and incubations from June 2010 indicate that propane and ethane consumption were the dominant microbial processes, with lesser rates of methane

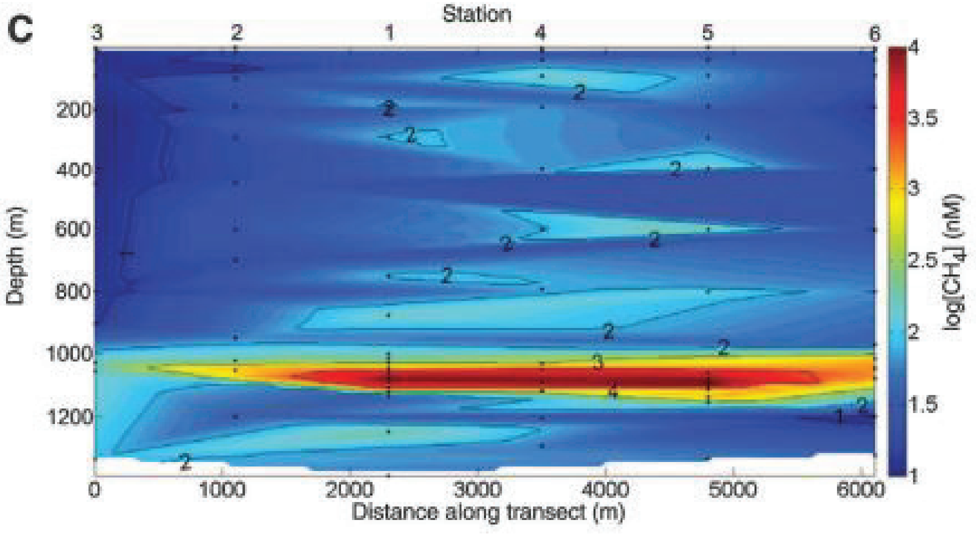

FIGURE 2.3 Contour plot of methane concentration taken to the southwest of the actively flowing Macondo well in June 2010. This figure illustrates a cross-section of an intrusion layer containing abundant dissolved hydrocarbons. Note the log scale. SOURCE: Figure 1C from Valentine et al., 2010.

consumption (Valentine et al., 2010). Several lines of evidence suggest that methane consumption followed in July and August 2010 (Du and Kessler, 2012; Dubinsky et al., 2013; Kessler et al., 2011a), though with some contention (Crespo-Medina et al., 2014, 2015; Joye et al., 2011b; Kessler et al., 2011b). Butanes and pentanes may have evoked a similar microbial response as ethane and propane (Rubin-Blum et al., 2017), though this assumption was not tested in the context of DWH. Spatial integration of oxygen anomalies from the depth of the intrusion layers in the months that followed DWH revealed a deficit that was similar in magnitude to the respiratory demand of discharged natural gas (Du and Kessler, 2012; Kessler et al., 2011a) consistent with its complete consumption by the bacterial community.

Because of its aqueous solubility natural gas serves as a potential tracer of deep ocean processes associated with well blowouts or other subsea discharge scenarios. During DWH, methane was proposed as a molecular target to calculate total discharge (Valentine, 2010), and ultimately an integrated subsea oxygen anomaly was used to estimate the total hydrocarbon respiration from the deep intrusion layers (Du and Kessler, 2012; Kessler et al., 2011a). Methane concentrations in the deep-sea intrusion layers were also found to correlate with observed anionic surfactant DOSS concentration, presumably because both are soluble in aqueous solution and dissolve rapidly (Kujawinski et al., 2011).

OIL FATE

Evaporation

Evaporation of lighter surface oil components occurs rapidly after an oil spill, which causes the loss of smaller, more volatile petroleum compounds with boiling points typically lower than that of *n*-pentadecane (Stout et al., 2017). Evaporation is quantitatively significant, and it is often the dominant process initially altering both the chemical composition and the physical properties of spilled oil. Typical crude oils lose 20%-50% of their mass from evaporation, whereas refined petroleum products can lose 75% and residual fuel oils typically lose ~10% of their mass (NRC, 2003, 2005). The loss of volatile petroleum compounds leaves behind an oil residue with higher density, lower solubility, and higher viscosity than the original oil, which makes it more likely to form water-in-oil emulsions and more difficult to disperse.

Evaporation reduces the water-soluble fraction of oil, and the loss of specific compounds such as benzene, toluene, ethylbenzene, and xylene (BTEX) to the atmosphere reduces the toxicity of the remaining oil to marine organisms. The transfer of BTEX compounds to the atmosphere, however, can pose an inhalation-related health risk to response workers and other exposed individuals and animals breathing air at the water surface (see Chapter 4). Dispersants were applied subsea during the DWH event with one justification being the reduction of VOCs surfacing around active response vessels (USCG, 2011). VOC concentrations were measured from surface vessels responding to well control between May 30 and June 10. Measurements taken from these vessels were summed and compared to SSDI hourly rates and hourly wind speeds to examine whether periods of low or no SSDI were followed by increased atmospheric concentrations of VOCs (Nedwed, 2017). While there were significant variations in measured VOC concentrations, there has not been sufficient analysis of the data collected to determine a relationship between the dispersant volume, VOC concentration, and environmental conditions at the DWH. However, some responders working at the wellhead area were reportedly convinced by their observations that dispersant use effectively reduced VOC levels (personal communications from Ken Lee, Rich Camilli; National Commission, 2011). It is challenging to make statistical correlations and draw robust conclusions from the available data because information regarding vessel location in relation to the well, surface oil slick, and prevailing winds was unavailable, and the tests performed were designed to inform immediate action, not for statistical validation. To further investigate SSDI and atmospheric VOC concentrations, additional VOC data collected from three surface vessels (Ryerson et al., 2012) was compared to model data generated for a representative day during the DWH event, after the riser was cut, when SSDI was being used (Gros et al., 2017). Although there were limitations in the VOC data available from response vessels (Nedwed, 2017), this study by Gros et al. (2017) supports the conclusion that the use of SSDI prolonged dissolution of water-soluble petroleum compounds (including BTEX) during the transport of oil to surface waters, resulting in fewer of the volatile oil components being present at the water surface for evaporation to take place (Gros et al., 2017). Rates of evaporation are further complicated by wind speed. For example, high wind speeds increase evaporation rates; but, they also promote dissolution of oil in the water column and diffusion of VOCs in the air, muddling the overall effect of wind (Crowley et al., 2018).

In addition to the compound-selective reduction in VOCs, SSDI during DWH is also assumed to have broadened the footprint of surfacing oil (Ryerson et al., 2012), with two important effects. First, the slow rise of small droplets allows for currents to shift the zone of surfacing oil away from the location of the wellhead and the intervention efforts. Second, a broadened surface expression equates to a dilution of atmospheric VOC concentration, other factors being equal. Both of these effects are important to response operations in that they reduce VOC exposure to personnel at the site of intervention, though not necessarily through a reduction in the quantity of surfacing oil.

The evaporation of oil is challenging to model because oils consist of thousands of different compounds, each with different physical and chemical properties. Early models focused on the loss of individual compounds as a function of their volatility (vapor pressure), wind speed, sea state, and temperature (e.g., Brutsaert, 1982; Sutton, 1934). Later models considered that there would be a decrease in the rate of evaporation as evaporation proceeds and so they incorporated a mass transfer coefficient dependent on wind speed (Stiver and Mackay, 1984). Comparisons of the model developed by Stiver and Mackay (1984) to experimental data indicated that the model performed well for the first 8 hours, but over longer periods of time, the model overestimated long-term evaporation (Bobra, 1992). Overestimation of evaporative losses of petroleum compounds arises from the presumption that the oil is a well-mixed phase; while true for thin slicks, however, this is not the case for thicker slicks. The thickness of the slick is important because evaporation from an oil slick is regulated by the diffusion of petroleum compounds within the oil to the oil-atmosphere interface, as opposed to diffusion across the air-boundary layer (Fingas, 2011, 2013, 2015). Further information and more detailed descriptions of these oil evaporation models are provided elsewhere (NRC, 2003, 2005).

Aerosolization

Bubble bursting and aerosolization are non-evaporative processes that transport oil into the atmosphere. Breaking waves entrain air into surface waters creating bubbles, which rise to the surface and burst to form marine aerosols in the atmosphere (Blanchard and Woodcock, 1980; Leifer et al., 2000). When surface waters are contaminated with oil, the aerosols formed contain these petroleum hydrocarbons. These aerosols may be comprised of ultrafine particles containing oil-derived VOCs with a higher toxicity compared to the spilled oil (Nel et al., 2006). Aerosolization also occurs as oil compounds that have evaporated into the atmosphere are oxidized to form secondary organic aerosols (SOAs). SOA formation generates compounds with lower volatilities that nucleate new particles or condense onto existing aerosol particles. Oil compounds of varying volatilities can be precursors for SOAs, including VOCs, SVOCs, and IVOCs (Robinson et al., 2007). The formation of SOAs from IVOCs present in surface oil slicks can be particularly significant owing to the slower evaporation rates of IVOCs and the greater time available for them to be transported and distributed over a wide sea surface area (de Gouw et al., 2011). Understanding the lifetime of individual petroleum compounds in the gas phase, and the formation and particle size of the SOAs they form (Brock et al., 2011), contributes to our overall understanding of their transport in air. Vertical dispersion and long-range atmospheric transport of SOAs is of particular interest because it has implications for air quality and public health both at the site of and downwind from an oil spill (Middlebrook et al., 2012).

Effective applications of dispersants to oil released into the environment is intended to increase the dispersion of oil compounds in the water column and reduce evaporation and subsequent aerosol formation. However, laboratory studies have shown that the application of dispersants to surface oil slicks can increase the number of aerosol particles produced by breaking waves by one to two orders of magnitude compared to untreated oil slicks (Afshar-Mohajer et al., 2018). The overall increase in aerosolization of oil compounds is attributed to an increase in the dispersion of oil in the water column as well as the flotation capacity of bubbles (Ehrenhauser et al., 2014). The applicability of these lab-based studies to real-world systems is yet to be determined.

Photochemical Oxidation

Photooxidation can significantly alter the composition of oil released into the aquatic environment (Fathalla and Anderson, 2011; Garrett et al., 1998; Payne and Phillips, 1985). Photochemical oxidation of oil occurs in sunlit waters via direct mechanisms, where light is absorbed by oil hydrocarbons, or by indirect mechanisms, where photosensitizers (e.g., dissolved organic matter) absorb light to produce reactive intermediates such as singlet oxygen or radicals that subsequently react with oil hydrocarbons (summarized in NRC, 2003, 2005). The chemical composition of oil is an important determinant for photochemical reactivity. The intensity and duration of light exposure is also important for evaluating the relative importance of photochemical oxidation to the fate of spilled oil. Light exposure is modulated by geographic location, season, local shading by cloud cover, and—in the case of dispersed oil—water depth and slick coverage.

Partial oxidation of oil hydrocarbons is the norm, producing compounds not originally present in the spilled oil (Aeppli et al., 2012). Some products of photooxidation are more water soluble than their hydrocarbon precursor(s) and can then be carried by water flow (Chapelle, 2001). Photomodification and photosensitization of polycyclic aromatic hydrocarbons (PAHs) have been found to increase the toxicity of residual oil following spills (Barron et al., 2003). Other compounds produced are high molecular weight products that form tar and gum-like residues (NRC, 1985, 2003, 2005), which increase the viscosity of oil and decrease the utility and efficacy of dispersants (Ward et al., 2018a).

Laboratory studies exposing a crude oil from Basilicata, Italy, to 100 hours of direct irradiation resulted in changes in the chemical composition of oil from photochemical reactions, with branched alkanes, linear alkanes, and aromatic hydrocarbons being photooxidized to different extents (D’Auria et al., 2009). Using a simulated freshwater environment, Yang et al. (2015) observed more rapid photooxidation of lower molecular weight alkanes than of the higher molecular weight compounds. In addition, PAHs were more susceptible to photooxidation than were alkanes, consistent with previous reports (D’Auria et al., 2009; Díez et al., 2007; Ebrahimi et al., 2007; Fathalla and Anderson, 2011; Garrett et al., 1998; Maki et al., 2001; Prince et al., 2003; Radović et al., 2014). Prince et al. (2003) also reported that most of the aromatic fractions were converted to resins and asphaltenes, while the saturates were unaffected. They further suggested that the photodegradation rate of PAHs was positively correlated to the number of aromatic rings and the extent of alkylation, which was inverse to biodegradation rates (Ebrahimi et al., 2007; Garrett et al., 1998; Prince et al., 2003; Stout et al., 2016; Wardlaw et al., 2011; Yang et al., 2016b).

Biodegradability and environmental persistence of the residual oil may be affected by changes in the physicochemical properties of aromatic compounds and their related components (King et al., 2014a; Lee, 2003). Photooxidation may increase biodegradation rates due to increased hydrocarbon bioavailability, or it may decrease rates due to toxic by-products, depending on the oil composition and response of the microbial community (Mallakin et al., 1999; Yang et al., 2017).

The DWH spill provided an opportunity to test existing conceptual models of photooxidation by tracking changes to the chemical composition of petroleum hydrocarbons in the environment. Petroleum hydrocarbons in oil residues were found to be converted to oxygen-containing products, including abundant hydroxyl and carbonyl functional groups, which accumulated in the residues within weeks of discharge (Aeppli et al., 2012). Hall et al. (2013) demonstrated that the oxidation process—especially photooxidation—is a major factor in the chemical changes of oil still left in the environment following the spill. Based on measured losses and altered asphaltenes from their experiments, Lewan et al. (2014) indicated that within the first 80 days of oil release from the DWH spill, a mean of 61 vol% of the spilled oil was lost from the surface. Reconnaissance experiments suggest that the composition changes occurred primarily as a consequence of the combined effects of photooxidation and evaporation rather than microbial degradation, dissolution, dispersion, or burning.

A study by King et al. (2014a) on photolytic and photocatalytic degradation of surface oil from the DWH spill indicated that the photodegradation of PAHs was rapid in the first few hours at the rate of 10% per hour. The process slowed to near zero after 6 days. While solar irradiation increased the evaporative loss of n-alkanes $< C17$, the loss of n-alkanes by photodegradation was not observed with the equivalent of 3 days of solar radiation. Bacosa et al. (2015) incubated surface water from the DWH site in quartz glass bottles under natural sunlight and temperature conditions to determine the contributions of photooxidation and biodegradation to the weathering of Light Louisiana Sweet crude oil. They reported that following the loss of lighter hydrocarbon components by evaporation, photooxidation rates exceeded that of biodegradation in the transformation of PAHs and alkylated PAHs in surface water oil sheens, while biodegradation was the main driver in the disappearance of alkanes. Compared to biodegradation, photooxidation increased transformation of 4-5 ring PAHs by 70% and 3-4 ring alkylated PAHs by 36%.

Photooxidation can produce tar and gum residues from surface oil when higher molecular weight products are produced through the condensation of peroxide and other free-radical intermediates (NRC, 1985, 2003), while some laboratory studies showed insignificant differences in oil density following irradiation (NRC, 2013; Short, 2013). It has also been suggested that the formation of microbial flocs in seawater, and the subsequent sinking of oily marine snow, may be associated with the exposure of light Macondo oil to ultraviolet irradiation (Chanton et al., 2014; Passow, 2016).

A recent study that merged field data from the DWH spill and modeling with laboratory experimentation found that oxygenation of petroleum hydrocarbons by sunlight occurred rapidly—with major compositional changes occurring in a matter of days (Ward et al., 2018b). During these environmental studies the chemical composition of oil residues changed substantially, with greater than half the mass of oil residues ultimately comprising oxygen-containing compounds. The oxygen-containing molecular products produced by photochemical transformation have been referred to as oxygenated hydrocarbons (or oxyhydrocarbons), and the process has been referred to as partial oxidation or oxygenation, as an attempt to distinguish this chemical route from complete mineralization to carbon dioxide (i.e., complete oxidation). The authors note that partial photooxidation at the sea surface could account for as much hydrocarbon as microbial biodegradation (to CO_2) in deep water, in contrast to the previous assumption that oxidation by sunlight is a relatively insignificant process for determining the fate and mass balance of oil.

By lowering oil-water interfacial tension (IFT) to enhance the breakup of oil into small droplets, dispersants may accelerate the photooxidation rates of spilled oil. Gong et al. (2015) reported that the presence of 18 and 180 mg/L of dispersant in seawater increased the first-order photodegradation rate of pyrene (at a test concentration of 60 μg/L) by 5.5% and 16.7%, respectively. Mechanistic studies suggested that the dispersant enhanced the formation of superoxide (O_2^-) radicals that contributed toward the photodegradation of the pyrene. Fu et al. (2017) investigated the photodegradation of pyrene with different dispersants. The results showed that increasing the concentration of either Corexit® 9500A or Corexit® 9527A enhanced the photodegradation of pyrene in comparison to SPC1000, which modestly inhibited the reaction rate. Under similar test conditions (18 mg/L dispersant; 60 µg/L pyrene, and 6 hours of incubation), the loss of pyrene was 89% for Corexit® 9500A, 85% for Corexit® 9527A, and 49% for SPC1000 compared to 55% without dispersants. Furthermore, they also noted that Corexit® 9500A was prone to photochemical decomposition, with > 95% degradation after 6 hours of solar radiation. They concluded that accelerated rates of photodegradation in the presence of Corexit® 9500A could benefit ecosystems through increased dissolution and decomposition of persistent hydrocarbons and higher biodegradation rates as well as reduced chemical toxicity. Zhao et al. (2016c) evaluated the response of different petroleum species within water accommodated oil prepared with Louisiana Sweet crude oil to photodegradation in the presence and absence of Corexit® 9500 at a DOR of 1:20. They concluded that under simulated sunlight, both n-alkanes and PAHs were susceptible to photodegradation, and the co-presence of oil PAHs and dispersant facilitated photodegradation of n-alkanes. In contrast to these previous studies, Ward et al. (2018a) reported that photochemical transformations over a simulated exposure period of 53 hours reduced the effectiveness of dispersant applications by 29%-34%. While this recent study is specific to the oil and laboratory exposure conditions employed (including the choice of glass type), it flags the possible importance of properly accounting for photochemical transformation in the dispersant application decision process, particularly in identifying temporal and spatial limits for dispersant efficacy at the sea surface, which is an especially difficult endeavor considering the assumptions that must be made with respect to complex on-water surface movements (see Figure 2.4).

Dissolution

Many compounds that comprise oil are slightly soluble in water. The solubility for a given oil hydrocarbon for a given solvent (e.g., seawater) is a function of its molecular properties and can be predicted using Linear Solvation Energy Relationships (Abraham et al., 2004; Goss, 2005). In general, aqueous solubility is quite low for hydrocarbons containing more than 10 carbons and increases among low molecular weight compounds, particularly those that are branched or contain aromatic functional groups. The extent to which any given oil hydrocarbon dissolves into an aqueous solution such as seawater is a function of its aqueous solubility but is modulated by various environmental conditions, including temperature, salinity, pressure, duration of exposure, chemical and physical properties of the oil, microscale characteristics of the interface through which it must travel to enter the aqueous phase, and its aqueous-phase concentration (Gros et al., 2017; Jaggi et al., 2017; Ryerson et al., 2011). Oil solubility and dissolution should not be confused here with the water-accommodated fraction of oil, which is an empirical quantity that includes both the dissolved and the suspended components.

Depending on the environmental context of its discharge, oil may experience prolonged exposure to water, allowing for dissolution of its more soluble compounds with or without the application of dispersants. Scenarios for which dissolution is an important consideration include subsea discharge; trapping of oil under ice; large entrainment of oil droplets in the upper water column, such as through breaking waves; and situations involving rapid sedimentation or flocculation. When oil is exposed to the atmosphere, such as at the sea surface, the extent of dissolution is dramatically reduced because many of the aqueous-soluble compounds are also highly volatile (as discussed above). The application of dispersant to oil, leading to dispersion in the water column, can reduce atmospheric exposure and increase aqueous exposure; thus, dissolution remains relevant for considering the fate of dispersed oil.

The effect of dissolution was pronounced in the environmental distribution of hydrocarbons resulting from the DWH event (Joye et al., 2011; Reddy et al., 2012; Ryerson et al., 2012; Valentine et al., 2010) because discharged oil traveled through more than 1,500 m of ocean water prior to

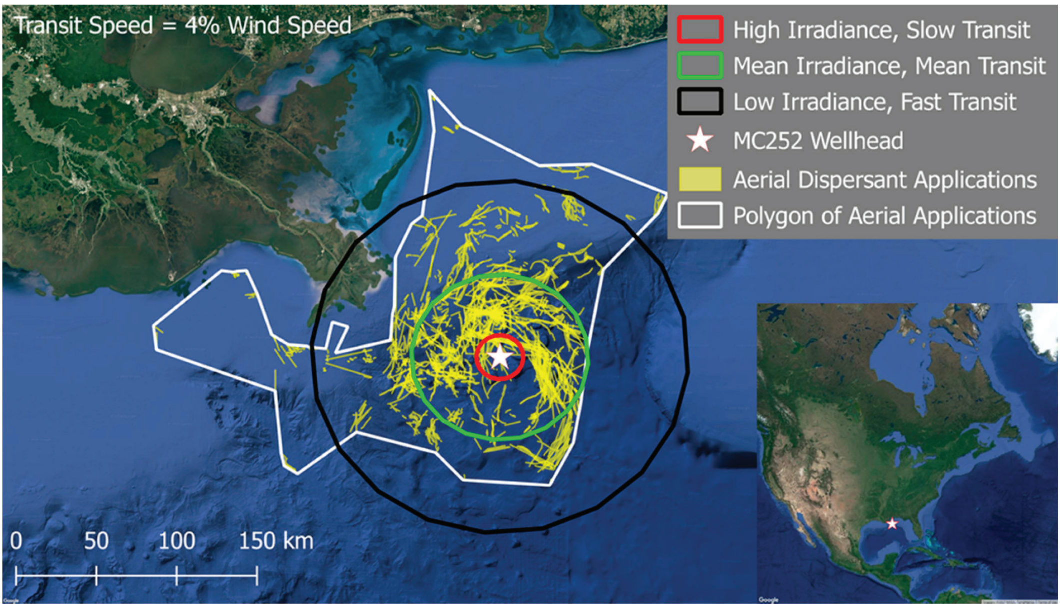

FIGURE 2.4 Assessing the effect of photochemical oxidation on the effectiveness of aerial dispersants applied in response to the *Deepwater Horizon* oil spill. The Macondo well is indicated by the white star; locations of the 412 flight paths for aerial dispersant applications are colored yellow and are outlined by the polygon in white. Each concentric circle represents the calculated distance from the well that surface oil traveled before photooxidation decreased dispersant effectiveness to < 45%, assuming high irradiance and slow transit speed (red inner circle), mean irradiance and transit speed (green intermediate circle), and low irradiance and fast transit speed (black outer circle). Irradiance levels were calculated by comparing the rate of simulated light absorption by oil in the laboratory versus natural sunlight on the Gulf of Mexico. Based on their analysis, Ward et al. (2018a) concluded that a substantial fraction of aerial applications targeted oil that had low effectiveness (i.e., < 45%), and this low effectiveness was principally driven by photochemical changes to the surface oil chemical properties. SOURCE: Ward et al., 2018a (available at https://pubs.acs.org/doi/10.1021/acs.estlett.8b00084; further permissions related to the material excerpted from this article should be directed to ACS Publications).

reaching the sea surface. The aqueous exposure resulting from this situation caused nearly complete dissolution of natural gas compounds and benzene as well as partial dissolution of several other alkanes, cycloalkanes, and BTEX compounds. The resulting oil hydrocarbon deficits in the atmosphere and enrichments in the ocean's subsurface (detailed in Figure 2.5) were important factors modulating the fate and effects of the discharge.

While the true aqueous solubility of oil hydrocarbons depends on their physical-chemical properties, hydrocarbons also partition to the water phase as microscopic aggregates, as considered in the "Dispersion" section below. The distinction between these phases is important not only for understanding fate and transport but also for understanding toxicological effects in the water column, as reviewed in Chapter 3. One emergent property of hydrocarbon dissolution in the presence of microdroplets is a buffering of dissolved hydrocarbon concentration caused by the presence of microdroplets suspended within the aqueous phase. For the case where droplets contain a greater mass of a soluble hydrocarbon than can dissolve in the aqueous phase, dilution of the solution will reduce the concentration of liquid-phase droplet hydrocarbons in proportion to the dilution. In a closed system, however, the aqueous-soluble components will reestablish equilibrium following the dilution, leading to no change in the aqueous-phase hydrocarbon concentration.

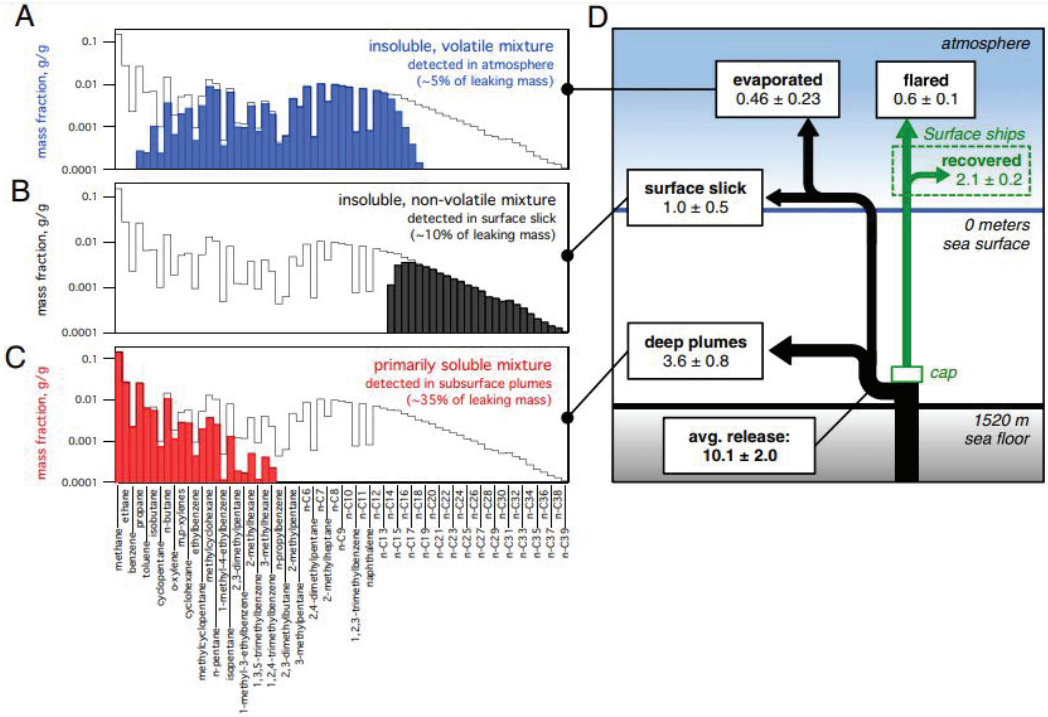

FIGURE 2.5 Evaporated hydrocarbon composition after 2 d (A; blue bars), surface oil slick composition after 2 d (B; black bars), and dissolved hydrocarbon composition (C; red bars). The leaking hydrocarbon composition from CH_4 through n-C_{39} (black line) is shown in each panel for comparison. (D) Schematic (not to scale) of hydrocarbon mass flows in the marine environment; values are calculated for June 10, 2010, in millions of kgs per day. This figure illustrates the molecular fractionation associated with dissolution and evaporation as occurred during the *Deepwater Horizon* oil spill. The figure comes from the primary literature (Figure 4 from Ryerson et al., 2012) and is based on data from disparate sources. The lack of mass balance reflects the different approaches and the uncertainties that arise. Reconciling these uncertainties is a focus of the original paper from which the figure was taken. SOURCE: Ryerson et al., 2012.

Subsequent dilutions may achieve dilution to extinction for the most highly soluble compounds, but the extent of dilution will vary based on compound solubility.

Hydrate Formation

Gas hydrates, or clathrates, are solid-phase materials that form spontaneously from water and hydrocarbon gases at high pressure and low temperature. For the context of this report, hydrates are thermodynamically stable at ocean depths greater than ~450 m and are thus most relevant to deep ocean discharge scenarios such as SSDI application. However, hydrate formation and stability also require high dissolved hydrocarbon gas concentrations and nucleation sites, the former of which are diluted by plume entrainment and mixing. This leads to stability near the point of discharge and instability owing to dilution that occurs as water moves away from the gas source. As reference, the highest concentrations of dissolved hydrocarbon gases measured in the DWH spill intrusion layers were ~100-fold below the requirement for gas hydrate stability (Joye et al., 2011; Valentine et al., 2010). Finally, hydrate formation requires a nucleation site. The combination of confinement (leading to high gas concentrations) and solid surfaces for nucleation led to the problem with hydrate buildup on several devices used in early attempts to cap the DWH blowout. Hydrate formation is thus most relevant to this study through its potential to affect processes near the point of discharge (e.g., see Box 2.1), with recent relevant studies in high-pressure laboratory facilities (Warzinski et al., 2014) and at natural seeps (Wang et al., 2016a). In the latter study, in situ high-speed imagery of seep bubbles near 1,000 m depth confirmed the formation of hydrate skins on gas bubbles from natural seeps, and field measurements indicate that mass transfer rates vary between the higher rates for clean and the lower rates for "dirty" bubbles (i.e., gas bubbles coated by another substance, such as hydrate) (Rehder et al., 2009; Wang et al., 2016a). The observation that mass transfer is not reduced below the dirty bubble rate may be due to cracks on the hydrate skin, as observed by Warzinski et al. (2014), and to the fact that the height to which the bubbles rise before they are completely dissolved depends mainly on the largest gas bubbles released from the seep.

In the DeepSpill field experiments, where oil was released as a plume at a depth of about 840 m, hydrates were not observed, even though it was noted that the methane dissolution rate in the water column was roughly half the value for clean bubbles which suggested that hydrate skinning might have been important (Johansen et al., 2003). On the other hand, it is possible that the bubbles were simply coated with natural surfactants (i.e., they were "dirty bubbles"), because surfactants (natural and in the form of chemical dispersants) reduce mass transfer when they coat bubbles. Evidence for hydrate formation during the DWH spill (oil released as a plume at a depth of about 1,500 m) is weak beyond the solid nucleation surfaces such as the cofferdam (see Box 2.1). Note that while a hydrate skin is sufficient to affect mass transfer, it has negligible thickness and thus little effect on bulk bubble density and rise velocity. The effect of dispersants on hydrocarbon fate and transport, due to any potential effect on hydrate formation, is not expected to be significant.

Emulsification

Emulsification of oil commonly occurs at the sea surface as a result of physical mixing of seawater into oil, creating a substance commonly described as mousse (depicted in Figure 2.6). The type and stability of the water-in-oil emulsion formed depends on the properties of the starting oil, in particular the viscosity as well as the proportion of high molecular weight components such as resins and asphaltenes. Environmental processes such as evaporation, dissolution, and photooxidation alter the chemical composition and viscosity of oil, thereby affecting the formation and stability of emulsions. Emulsified oil is a semisolid material with considerably different physical properties and characteristics than those of the original liquid oil. Information regarding the formation and stability of emulsions is detailed elsewhere (e.g., NRC, 2005).

Low molecular weight oil compounds are lost in the environment by processes such as evaporation and dissolution, leading to an enrichment in the relative concentration of emulsifying agents such as resins and asphaltenes, which enhance the formation of stable emulsions (Fingas et al., 2000). Photooxidative processes produce compounds that can act as emulsifying agents (NRC, 2005). Considering these environmental factors, the size and thickness of oil slicks on the sea surface are important for emulsification, because it relates directly to how much oil is exposed to the atmosphere and water and subsequently how much evaporation, dissolution, and photooxidation can occur. Other environmental factors influencing emulsification include temperature (emulsification occurs more rapidly at lower temperatures) and the energy of mixing in the marine environment (increased energy accelerates emulsification).

Emulsification subsequently reduces oil evaporation and dissolution (Ross and Buist, 1995; Xie et al., 2007). The increase in water content, density, and volume of emulsified oil is also important and has implications for the fate and recovery of oil in the environment. The most substantial change in physical properties to oil when it is emulsified is the increase in its viscosity (Davies et al., 1998; Fingas et al., 1994), which is particularly relevant as it may hinder oil dispersion both with and without the use of dispersants. Dispersants may be used on emulsified oil, but they are

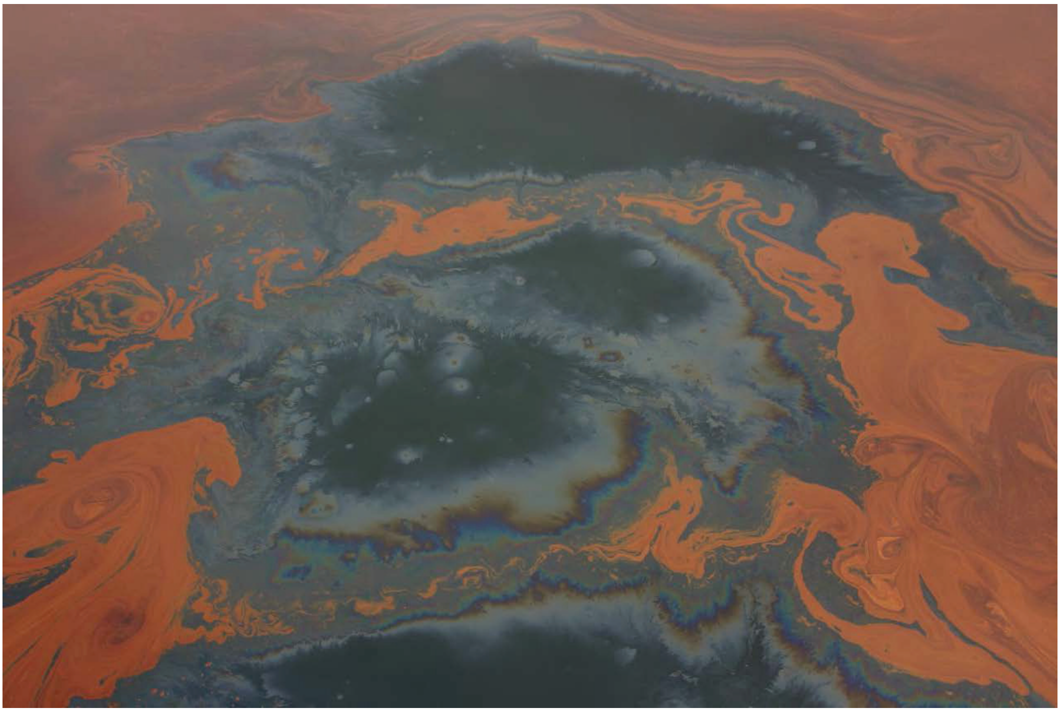

FIGURE 2.6 Water in oil emulsion (mousse, colored orange-brown) as observed during the *Deepwater Horizon* oil spill. This image was taken from the deck of a ship, approximately 3 m from the ocean's surface. Photo credit: David L. Valentine.

potentially less effective and may require a higher DOR (NRC, 2014). Emulsion viscosity and the type of dispersant applied determine the dispersant effectiveness, with emulsions composed of higher viscosity oils being the most difficult to effectively disperse (Belore et al., 2008).

Solid-Phase Interactions

Upon exposure to the ocean or other aquatic environments, petroleum hydrocarbons may contact various solid or semisolid phases, including mineral and biological materials, and may induce changes within such materials. Such interactions have been studied for select scenarios, which are considered in this section. These may include adhesion to a bulk phase; aggregation with mineral or biological particles (Lee, 2002); conversion to petroleum-derived bacterial flocculent (Bælum et al., 2012; Hazen et al., 2010; Valentine et al., 2014); and flocculation with marine snow or other would-be sediment particles (Passow, 2014). Importantly, such interactions are situational. The formation of oil-particle aggregates (OPAs), for example, requires proximity to a source of relevant particles, which provides a geographic constraint. The chemical properties of the oil also impact deposition and preservation, as exemplified by a fallout plume of heavy oil from natural seeps (Farwell et al., 2009) and the pattern of long-term geologic preservation for oil-stained foraminiferal tests in (anoxic) marine sediments (Hill et al., 2006). This section focuses on key processes by which petroleum hydrocarbons interact with particles and on the potential for dispersant application to affect these processes. Ultimately, these interactions structure transport of oil to the benthic environment, inclusive of sediment deposition, benthic exposure, and burial. OPAs are considered first, followed by marine oil snow (MOS).

Oil-Particle Aggregates (OPAs)

The term “oil-mineral aggregate” (OMA) was first used by Lee et al. (1998) to describe the observed formation of microaggregates between fine-grained sediment and oil. It was initially described as “clay-oil-flocculation” by scientists as a mechanism that accounted for the loss of stranded oil from intertidal low-energy coastal environments impacted by the *Exxon Valdez* spill (Bragg and Owens, 1995; Bragg and Yang, 1995). While OMA was used extensively in studies working on oil-mineral interactions (Ajijolaiya et al., 2006; Khelifa et al., 2002; Lee, 2002; Niu et al., 2011; Stoffyn-Egli and Lee, 2002), the terms “oil-sediment aggregate” (Bandara et al., 2011; Cai et al., 2017) and “oil-suspended particulate matter aggregates” (Gong et al., 2014; Loh et al., 2014) have also been used to describe the natural interaction between oil and suspended particulate material that may also include organic matter. As detailed in the next section, aggregates of oil with organic matter (e.g., bacteria, phytoplankton, dead cells, or extracellular polymers) have been described as “marine oil snow” (Daly et al., 2016; Fu et al., 2014; Passow and Ziervogel, 2016; Passow et al., 2012). OPAs has now been used to account for interactions of oil with both inorganic and organic material (Fitzpatrick et al., 2015; Zhao et al., 2016b, 2017c) and was defined by Gustitus and Clement (2017) as a term to describe aggregates on a scale of 1 mm or less for nearshore environments. The relationship across these terms is depicted in Figure 2.7.

Oil-particle interactions alter the buoyancy of oil droplets because the OPAs formed are negatively or near neutrally buoyant, allowing their transportation in the water column and eventual sediment deposition (Bragg and Owens, 1995; Lee et al., 2003). OPAs suspended in the water column or resting on the bottom can be subsequently carried upward by larger currents, enabling

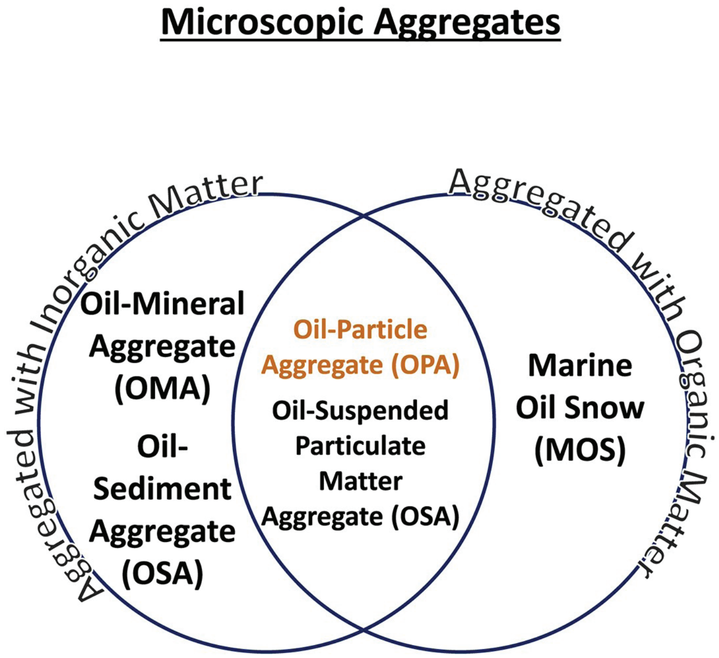

FIGURE 2.7 Summary of terminologies used for describing different types of OMAs. SOURCE: Gustitus and Clement, 2017.

oil to be transported from one environmental compartment to another (Fitzpatrick et al., 2015; Waterman and Garcia, 2015). The interactions of oil droplets and particles following oil spills is now considered to be an important process in the natural attenuation of oil spilled at sea (Bragg and Owens, 1995; Bragg and Yang, 1995; Lee, 2002).

OPA formation depends on the properties of the oil (oil type and concentration, droplet size), particle size, shape, and concentration as well as density and organic matter content and the ambient conditions (temperature, water salinity, mixing energy) (Ajijolaiya et al., 2006; Frelichowska et al., 2010; Gong et al., 2014; Gustitus et al., 2017; Lee, 2002; Payne et al., 1989; Stoffyn-Egli and Lee, 2002).

Because OPA formation prevents oil droplets from recoalescing and may keep the oil-water interfacial area suspended within the aerobic zone of the water column over a longer period of time, hydrocarbon dissolution and oil biodegradation rates are enhanced (Ajijolaiya et al., 2006; Aveyard et al., 2003; Gong et al., 2014; Khelifa et al., 2002; Lee et al., 1997; Weise et al., 1999). Laboratory (e.g., Stoffyn-Egli and Lee, 2002; Wang et al., 2011; Zhang et al., 2010) and shoreline data (e.g., Bragg and Owens, 1995; Lee et al., 2003) have shown that OPAs enhance the dispersion of oil and can be considered the basis for an oil spill countermeasure strategy (e.g., surf washing) for oil stranded in the shore zone (Lee, 2002; Owens and Lee, 2003).

Oil dispersion is positively correlated to the formation of OMAs, as smaller oil droplets require fewer suspended particles to form OMAs (Gong et al., 2014; Gustitus et al., 2017). Zhang et al. (2010) found smaller particle sizes of solids with larger specific area favored the formation of OMAs. It was reported that the formation of OMAs was negligible when the particle size was larger than 10 microns (μm). When the particle size was less than 2 μm, OMAs were readily formed. The lowering of oil-water interfacial tension by the addition of dispersants has been linked to the formation of smaller oil droplet size (Li et al., 2008b; Zhao et al., 2014b) and higher effectiveness values for oil dispersion and formation of OMAs (Khelifa et al., 2008).

The surface properties of the particles also play an important role in determining the size and the type of OMAs as well as the fraction of oil that can be dispersed as OMAs. Wang et al. (2011) examined the interactions between oil and three types of solids: namely, kaolin, modified kaolin, and diatomite. They found that solids with higher hydrophobicity have more oil-mineral attraction. The enhancement of the surface hydrophobicity of these naturally occurring minerals by addition of dispersants or treatment with cetyltrimethyl ammonium bromide improved the effectiveness of the OMA formation (Chen et al., 2013; Lee et al., 2012; Wang et al., 2011; Zhang et al., 2010).

Changes in oil characteristics from natural weathering processes may also affect the formation of OMAs. Studies by Bragg and Yang (1995) and Wood et al. (1998) suggested that weathered oils tend to form OMAs more readily. In contrast, Guistitus et al. (2017) recently reported that formation of OMAs was substantially hindered when oil was weathered. Their findings suggested that the increased viscosity associated with the weathering process outweighed the increased fraction of polar or charged compounds.

Hydrodynamic conditions and the associated energy dissipation rates are important factors governing the dispersion of oil slicks (Li et al., 2008a) and thus the formation of OMAs (Ma et al., 2008; Omotoso et al., 2002; Sun et al., 2010, 2014; Wincele et al., 2004). In general, higher mixing energy favors the formation of smaller OMAs and reduces mixing time for the formation of OMAs (Sun and Zheng, 2009; Sun et al., 2010, 2014). Once OMAs are formed, they tend to be relatively stable against continued turbulence. Zhao et al. (2017c) recently reported, however, on the breakdown of OMAs under turbulence and the formation of larger OMAs composed of multiple small droplets. Temperature affects the formation of OMAs primarily by influencing the viscosity and adhesion properties of oil. The formation of OMA under low temperature conditions (–1-4°C) has been observed in laboratory batch scale tests (Lee et al., 2012; Wang et al., 2013); pilot scale flume tank (Jézéquel et al., 2018); and field scale in ice-infested waters in the St. Lawrence Estuary under Arctic conditions (Lee et al., 2009, 2011). Elevated temperatures, too, have been found to favor the formation of OMAs (Lee et al., 2012; Stoffyn-Egli and Lee, 2002; Wang et al., 2013).

The addition of dispersants has been primarily demonstrated as a synergic practice for OMA-induced oil dispersion; Mackay and Hossain (1982), however, found that chemical dispersion of oil reduces its tendency to associate with mineral matter. Guyomarch et al. (1999) demonstrated that the dispersant Inipol IP90 favored the formation of OMAs in a wave tank experiment. Li et al. (2007) reported the combination of mineral fines and dispersants (Corexit® 9500) significantly increased the dispersion efficiency and formed smaller OMAs. Khelifa et al. (2008) found with addition of dispersant, the oil sedimentation was three to five times higher than the control without dispersant at sediment concentrations of 25 and 50 mg/L. The enhancement was not significant for sediment concentrations higher than 100 mg/L. Wang et al. (2013) tested the synergic effect of dispersant on the formation of OMAs in a low temperature environment. They also verified the synergic effects especially for viscous oil IFO-40 and found that Corexit® 9500 performed better than Corexit® 9527. They suggested that optimal oil-to-dispersant and oil-to-mineral ratios could be found, and that higher ratio of dispersant led to small, spherical OMAs with greater negative bouyancy. The study further suggested that the combined minerals and dispersants may maximize the overall performance of the response, especially under cold conditions when oil becomes harder to disperse with exclusive use of either agent. The settling rate of OMAs has been reported to be correlated with the viscosity/density of the crude oil (Omotoso et al., 2002). Furthermore, higher concentrations of oil droplets in the mixing system were associated with the observation of higher ratios of solid OMA/droplet OMA (Stoffyn-Egli and Lee, 2002).

The concentration of particles affects the effectiveness of OMA formation (Ajijolaiya et al., 2006; Sun et al., 2010). O'Laughlin et al. (2017b) found that the OMAs were formed with larger size when the concentration of the particles was increased. Zhao et al. (2016b) developed the A-DROP model to predict the formation of OPA based on particles depositing on the oil droplets (i.e., based on Type I OPA). The A-DROP model was based on population balance equation for three entities: the oil droplets, the particles, and the OPA. The disadvantage of the model is that it is computationally demanding. Its advantage is that it accounts for other characteristics on OPA formation, including the effect of the coated area on the droplet surface as well as hydrophobicity and the particle-to-droplet-size ratio.

The surface coverage assumed by these works came under scrutiny in the work of Zhao et al. (2017c), who, using confocal microscopy, showed that the particles with plate morphologies penetrate the droplets and do not rest on their surface. In addition, the study revealed that the OPA is unstable, and that it would fragment within 12 hours to form much smaller OPAs (going from 30 μm in diameter to less than 5 μm). This raises the possibility of using particles to mitigate an oil spill at locations where dispersants cannot be used.

OPA formation has been associated with previous oil spills such as *Tsesis*, Ixtoc I, and others (Jernelöv and Lindén, 1981; Johansson et al., 1980; Teal and Howarth, 1984; Vonk et al., 2015). The magnitude of the DWH and the corresponding efforts to understand the fate of the spilled oil, however, have provided unique insights into the formation mechanisms and quantity of different OPAs as well as the spatial footprint of the sedimented oil (Bagby et al., 2017; Brooks et al., 2015; Chanton et al., 2014; Daly et al., 2016; Passow, 2016; Romero et al., 2015, 2017; Schwing et al., 2017; Stout et al., 2016; Valentine et al., 2014). Estimates of the quantity of oil reaching the seafloor range from 2% to 11% of the total oil released and not recovered (Chanton et al., 2014; Romero et al., 2017; Valentine et al., 2014).

Marine Oil Snow (MOS)

During and briefly after the DWH oil spill, MOS was observed in the vicinity of the wellhead followed by its disappearance from the surface after a month (Passow et al., 2012). Based on these observations, a significant fraction of the oil components deposited on the seafloor is hypothesized to have arisen from a transport process known as Marine Oil Snow Sedimentation and Flocculent Accumulation, or MOSSFA, whereby oil is captured by marine snow, which in turn traps other particles such as minerals and other organic matter (Kinner et al., 2014; Montagna et al., 2013; Passow et al., 2012; Romero et al., 2015; White et al., 2012), as outlined in Figure 2.8 (Daly et al., 2016; Romero et al., 2017). For a 4- to 5-month period during and after the oil spill, Brooks et al. (2015) interpreted the sediment accumulation rate through MOSSFA to exceed the pre-spill sediment accumulation rates. By using biomarker-hopanes as tracers, Valentine et al. (2014) estimated that 1.8%-14% of the oil was transported to the seafloor through, for example, bacterial-induced flocculation in the deep ocean intrusion layers. Chanton et al. (2014) estimated the percentage of

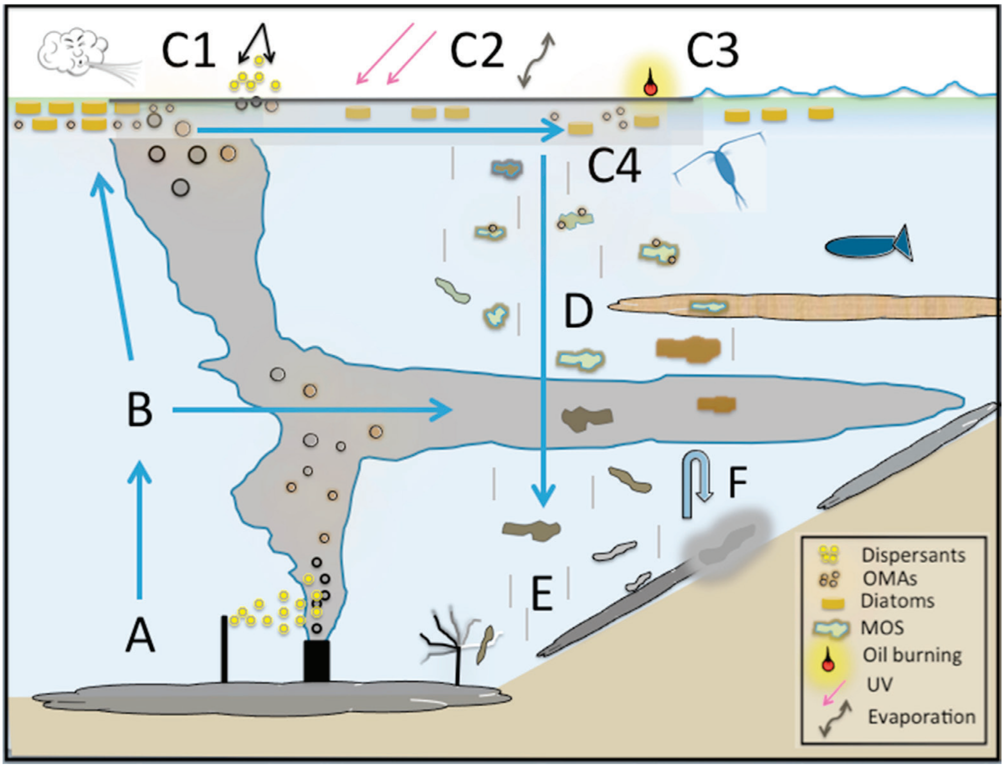

FIGURE 2.8 Conceptual diagram of MOS-related processes from the source of oil discharge to the fate of hydrocarbons in sediments. (A) shows the release of oil at the wellhead and application of dispersants and (B) represents rising oil droplets and gas bubbles and the formation of a deep oil plume. (C1-C4) show surface processes influencing the formation of MOS: (C1) illustrates wind impacts, a diatom bloom, and application of surface dispersants, (C2) shows oil transformation due to UV light and evaporation, (C3) depicts the role of aerosols and oil burning in creating new material sources, and (C4) shows processes impacting sinking MOS particles in surface waters and as particles sink through (D) a benthic nepheloid layer and deep oil plumes. (E) shows benthic sedimentation of MOS and flocculation onto corals, and (F) represents resuspension of oiled sediments due to turbulence. SOURCE: Daly et al., 2016.

sunken oil at 0.5%-9% by radiocarbon analysis. Schwing et al. (2017) identified two regions with heavy MOS and estimated the total sedimentary spatial extent of MOSSFA from 12,805 to 35,425 km^2. By using sediment trap and hopane-based biomarkers, Stout and German (2018) estimated that more than 76,000 barrels (bbl) of oil sank over an area of approximately 7,600 km^2. It is important to note, however, that the use of recalcitrant hydrocarbon compounds to calculate a volume of crude oil remaining in the environment provides a normalized value that excludes the action of weathering processes and is therefore an overestimate. Other processes have also been proposed to account for deposition of oil to the seafloor, including sinking of burn residues (Stout and Payne, 2016a) and adhesion of oil to clay and barite that comprised drilling muds/fluids (Stout and Payne, 2016b) used for well intervention.

Factors controlling the creation of depositional events, in the presence of oil and dispersants, are varied and their interactions complex (Daly et al., 2016; Gong et al., 2014). Passow et al. (2012) speculated that the MOS was formed through the interaction of three mechanisms: (1) production of mucous webs made of extracellular polymeric substances (EPSs; a mucilaginous material comprised predominately of carbohydrates and protein), especially the sticky transparent exopolymeric particles through the activities of bacterial oil-degraders associated with the surface oil layer; (2) formation of OMAs that integrated with the mucous webs upon collisions; and (3) incorporation of phytoplankton into aggregates. Oil and dispersants are implicated in the formation of the EPSs, which act as a matrix upon which OPAs, dead phyto- and zooplankton, fine clay particles, burned oil and soot residues, and bacteria can accumulate (Bælum et al., 2012; Daly et al., 2016; Fu et al., 2014; Hazen et al., 2010; Passow, 2016; van Eenennaam et al., 2016). The EPSs are thought to be synthesized and excreted as a stress response of surface-dwelling biota (e.g., phytoplankton, zooplankton, and bacteria) possibly to form a physical and chemical boundary limiting direct contact of potentially toxic oil compounds and dispersants to their cell membranes. Passow (2016) investigated the mechanisms and placed the focus on the impact of oil type, photochemical aging of oil, and the presence of phytoplankton and dispersants. Laboratory studies indicate that in the presence of dispersants and oil, phytoplankton and bacteria increased quantity and changed the properties of the EPS(s) and marine snow they produced (Fu et al., 2014; Hatcher et al., 2018; Passow, 2016; van Eenennaam et al., 2016), although some inhibition of OPA formation in the presence of weathered crude oil has also been observed under certain conditions (Passow et al., 2012, 2017). The observed phenomena were not specific to the Gulf of Mexico region; similar results have been observed in field experiments conducted during the winter in the Faroe-Shetland Channel (Suja et al., 2017) and experiments with bacteria from the deep ocean (Bælum et al., 2012). Figure 2.9 illustrates the MOSSFA-like flocculation process that occurred near the wellhead following the DWH spill.

Fu et al. (2014) noted that the addition of dispersant increased the total n-alkane adsorbed on MOS by 1.23-fold, which increased its buoyancy over control samples without dispersant treatment. Kleindienst et al. (2015b) found that the addition of dispersants and nutrients induced a rapid onset of MOS formation (5 days versus 2 weeks in the treatment without dispersant and nutrients). The sizes of the MOS in the former case were much larger (2 cm versus 0.5 cm). Without nutrients, the addition of dispersants changed the morphology of MOS from fractal-looking aggregates to aggregates associated with filaments (Kleindienst et al., 2015b). Furthermore, bacteria belonging to the genus *Colwellia* were found to be enriched in all dispersant-amended treatments. Suja et al. (2017) echoes the finding that dispersants triggered the formation of MOS, which is magnified by the addition of nutrients. On the other hand, Passow (2016) found that the addition of dispersants inhibited the formation of MOS. In this particular case, however, results could have been influenced by the fact that test oil had been amended previously with dispersants and, therefore, further addition of dispersants may have elicited an overdose response.

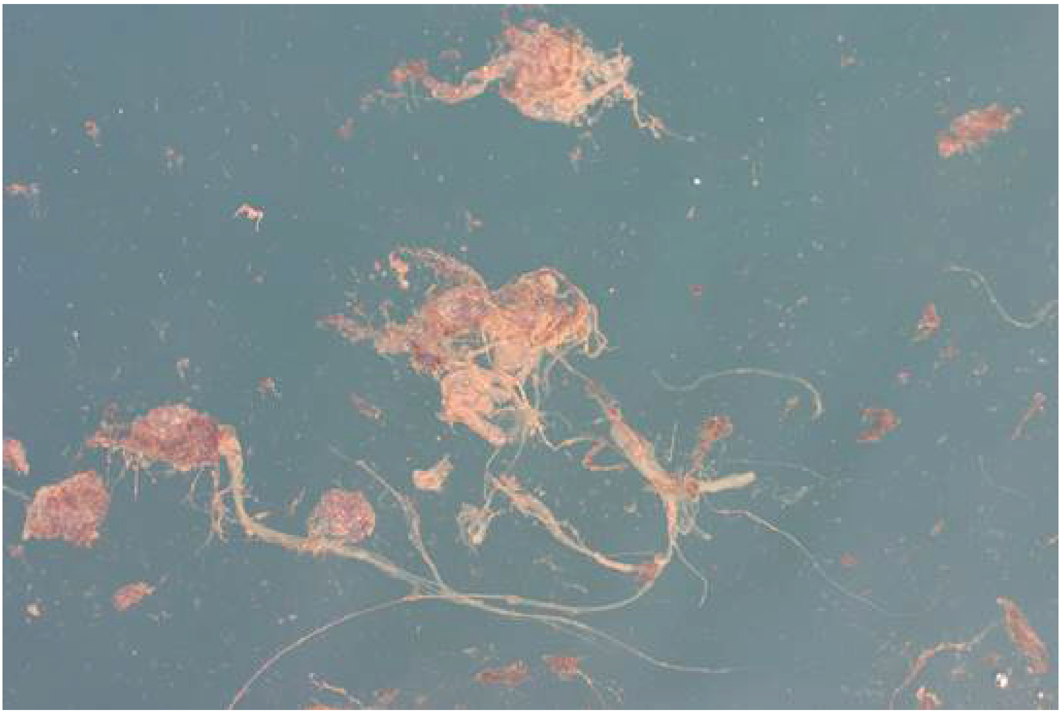

FIGURE 2.9 Image of oil flocculent at the ocean surface from the DWH event. The width of the image is approximately 1 m. Photo credit: David L. Valentine.

Brakstad et al. (2018a) recently completed a comprehensive review of literature related to marine snow studies following the DWH oil spill, with a focus on the use of oil spill dispersants and the formation, fate, and transport (i.e., sedimentation) of oil-related marine snow (ORMS). Contrary to the literature supporting the MOSSFA hypothesis, they concluded that the contribution of dispersant or any treatment to the formation of ORMS during the DWH spill could not be determined from the results of existing laboratory studies as experiments were only performed at high oil concentrations that did not take into account rapid dilution within the open sea. In summary, studies are still required to determine ORMS processes at oil concentrations under environmentally realistic conditions wherein dispersed oil plumes are expected to rapidly dilute to concentrations below 1 ppm (Lee et al., 2013a; Prince et al., 2016).

For the case of DWH, a potential sequence of events is provided in Figure 2.8 as a conceptual model specific to formation and deposition of MOS. According to this hypothesis, nutrient flow to nearshore waters was enhanced by flooding of marshes with fresh water to prevent oil washing ashore (Bianchi et al., 2011; Daly et al., 2016; Passow, 2016). An enhanced nutrient supply from this remedial strategy and inflow from the Mississippi River system may have stimulated phytoplankton blooms (Hu et al., 2011; O’Connor et al., 2016) and provided large quantities of fine-grained, clay-based particles into the nearshore oceanic environment. The addition of large quantities of surface-applied dispersants to weathered crude at the surface apparently induced EPS formation and helped form large OPA particles, up to tens of cm (Daly et al., 2016; Fu et al., 2014; see Figure 2.8). The clay particles entrained within OPAs helped ballast the particles, accelerating sinking rates and increasing mass accumulation rates over background levels (Romero et al., 2015, 2017).

Multiple studies have investigated the ecological impacts of enhanced mass accumulation of sedimented oil on deep-sea benthic organisms. Declines in macro- and meiofauna (Montagna et al., 2013; van Eenennaam et al., 2018) as well as mortality and morbidity of deep coral communities (Fisher et al., 2014; White et al., 2012) have also been documented within the Gulf of Mexico.

Although various mechanisms, including MOSSFA, have been postulated to transport oil to the floor of the deep ocean, the relative importance of these mechanisms has not been quantified for the DWH spill and remains difficult to predict for other discharge scenarios. Given the paucity of sampling that occurred during the active depositional phase of the DWH spill, latent deposition mechanisms could have gone unnoticed; for example, those associated with apparent blooms and mortality of deep ocean filter feeders. Nonetheless, the conceptual model of Daly et al. (2016; see Figure 2.8) comports well with a number of mechanisms related to MOSSFA identified in both field collections and laboratory experiments, and other identified mechanisms remain viable as well (Gros et al., 2017; Stout and Payne, 2016a,b; Valentine et al., 2014). However, critical details leading to significant depositional events have not been quantified. Key uncertainties include the concentrations of oil, dispersants, nutrients, plankton densities, bacterial growth response, and sediment particles/fractions. To close this gap, Daly et al. (2016) have identified a research framework to better elucidate deposition specific to MOSSFA-type scenarios.

Biodegradation

The diverse assortment of chemical compounds comprising petroleum provide a potential source of energy and carbon to microbes that have evolved for their consumption. The environmental relevance and distribution of hydrocarbon biodegradation is underscored by the diversity of microbes capable of consuming hydrocarbons as a source of carbon and energy—including at least 175 genera in 7 phyla of bacteria and archaea, in addition to eukarya such as fungi (McGenity, 2018). The focus here is on biodegradation activities for petroleum discharged to the ocean, with particular emphasis on the potential interplay between chemical dispersant and the responsible microbial community.

While many microbial taxa have evolved to consume petroleum hydrocarbons, numerous variables—chemical, environmental, and situational—serve to control the rate and extent of degradation for any given circumstance. The large number of genera hosting hydrocarbon-degraders is itself a direct reflection of the evolutionary pressure imposed by these variables. Many of the key variables that control biodegradation have been reviewed previously (Leahy and Colwell, 1990; NRC, 2003), and studies have demonstrated a spectrum of effects when dispersant is provided to hydrocarbon-degrading bacteria (Kleindienst et al., 2015b; NRC, 2005; Prince et al., 2016). The focus here is on recent findings that inform the relationship between petroleum hydrocarbon biodegradation and the application of chemical dispersant, particularly for realistic encounter scenarios. Box 2.2 specifically considers the issue of biodegradation and SSDI, drawing on observations from DWH.

Upon discharge or exposure to the environment, petroleum hydrocarbons become available for biodegradation. The first step toward biodegradation is the encounter between the would-be consumers and their substrate, which will depend on the abundance, distribution, and metabolic status of the seed population as well as the physical and chemical properties and spatial distribution of the hydrocarbons. Following an encounter, the microbial population must adapt to consume the available substrate, and growth of the community will occur, anchored by the microbes that adapt most quickly to the ambient conditions. The early stages of microbial community growth and development are expected to have minimal impact on the petroleum hydrocarbons, because seed populations must generally grow by order(s) of magnitude to induce a measurable change, as modeled for the DWH spill by Valentine et al. (2012). The early stages of biodegradation are highly relevant for the purposes of this report, however, because dispersants are typically applied to fresh

BOX 2.2
Biodegradation and SSDI

This box highlights the complexities of biodegradation in the context of SSDI by addressing specific questions relating to the DWH spill response.

How quickly do deep-sea bacteria populate oil?

Even for deep Gulf of Mexico waters that are exposed to an abundance of hydrocarbons through natural seepage, the bacterial population is sparse. Of the bacteria that are present, only a small percentage are potentially capable of hydrocarbon oxidation (King et al., 2013). The native cell density of would-be hydrocarbon degraders in the deep Gulf of Mexico has been estimated on the order of 10-1,000 per milliliter of seawater, whereas the resulting blooms in response to the DWH release contain on the order of 10,000-100,000 per milliliter (Hazen et al., 2010; Valentine et al., 2012). The baseline abundance and activity of hydrocarbon degraders is low, and a significant (orders of magnitude) growth response is needed to measurably alter hydrocarbon concentrations based on common analytical methods for quantification of hydrocarbon concentration (Bagby et al., 2017; Hazen, 2018; Hazen et al., 2016). Athough the early stages of microbial blooms may be evident, there is a lag in the corresponding biodegradation. In deep ocean waters, blooms can take weeks to mature, and they are dependent on the abundance and status of the seed population; the suitability of the environment for bacterial growth (limiting nutrient—P, Fe, N—availability); and the availability of substrate, water mass mixing, and the extent of predation (Hazen et al., 2016). Once populations are established, hydrodynamics also become important as a mode of diluting hydrocarbons and bacteria, renewal of oxygen and limiting nutrients, and seeding of bacteria to unexposed waters. The latter was termed dynamic autoinoculation in the context of DWH (Valentine et al., 2012).

Did SSDI contribute to biodegradation in the deep ocean?

Available evidence from DWH indicates that deep intrusion layers were preferentially enriched in soluble hydrocarbon components compared to the liquid oil droplets. Evidence from various sources is compiled by Gros et al. (2017) and indicates that ~5% or less of the liquid oil was trapped in the deep intrusion layers. Evidence preceding the onset of SSDI is similarly consistent with low percentages of liquid oil in the deep intrusion layers. These observations are consistent with a scenario in which SSDI reduced the droplet size distribution sufficiently to slow droplet rise rates and thus affect surfacing location, but not so much as to trap more than approximately 5% of the liquid oil as suspended microdroplets. By this analysis, the effect of SSDI on biodegradation of liquid oil in the subsurface intrusion layers is minor insomuch as only a small fraction of liquid oil was trapped in the layers with and without SSDI. However, because of the reduced droplet size and associated rise rates, SSDI could have led to an increase in biodegradation in the subsurface waters above the intrusion layer (Lofthus et al., 2018; Ribicic et al., 2018).

Did SSDI trap aqueous-soluble hydrocarbon substrates in the deep ocean?

No formal tests were conducted during DWH to determine if SSDI impacted the fraction of aqueous soluble hydrocarbons—potential substrates for biodegradation—trapped in the ocean's interior, leaving only inferential and modeling studies. Observations indicate that the most aqueous-soluble compounds, including the natural gases, benzene, and toluene, effectively dissolved in the deep ocean. What is less certain is the impact of SSDI on the dissolution extent for hydrocarbons of lesser aqueous solubility, such as xylene, ethylbenzene, cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, naphthalenes, and flourene, each of which is a potential bacterial substrate. During the period of active SSDI, these compounds were partially dissolved (Ryerson et al., 2012), but no equivalent data are available for the period of the spill preceding regular SSDI. The extent of dissolution is expected to increase with SSDI because of the increased surface area and rise time for the smaller droplets. By this argument, greater surface area and slower rise velocities would provide for increased dissolution in the SSDI scenario and thus more substrate for biodegradation.

BOX 2.2 Continued

Is droplet surface area a limiting factor for biodegradation?

Bacteria must encounter their substrate to enable ingestion. For aqueous-soluble hydrocarbon substrates, bacteria may be free floating, oil attached, or attached to another solid phase and can encounter substrate that is diffusing through the aqueous phase. For those bacteria that consume liquid oil, substrate attachment is an important consideration. For these latter bacteria, surface area is generally considered as a metabolic limitation, with adaptations including direct adhesion to hydrophobic surfaces (see Figure A) and the biosynthesis of surfactants. Despite adaptations, observations from oiled sediment at DWH support the idea that biodegradation is more rapid for small accumulations of oil and slower for larger accumulations (Bagby et al., 2017). However, it is important to note that the size of inferred droplets from these studies (Bagby et al., 2017) are orders of magnitude larger compared to the size range for microdroplets (e.g., < 70 mm). Brakstad et al. (2014, 2015) and others have shown that biodegradation of Macondo oil is faster in smaller droplets and in dispersion flumes.

What happened to the dispersant from SSDI?

Samples collected from the DWH intrusion layers contain the anionic surfactant DOSS, which is aqueous soluble and thought to have dissolved from the oil droplets to the ocean commensurate with intrusion layer formation (Kujawinski et al., 2011). Other components of the dispersant are presumed to have behaved analogously, according to their aqueous solubility. The conclusion from these observations is that dispersant components fractionated in the deep sea, partially separating from the rising droplets. Once dissolved in the deep intrusion layers DOSS was diluted by mixing, rather than experiencing rapid biodegradation (Kujawinski et al., 2011), whereas nonionic surfactants that reached the sea surface would have been subject to various degradation processes, including ester hydrolysis and biodegradation (Choyke, 2018). Evidence of conditional persistence in the deep sea comes from the identification of DOSS mixed with oil and attached to deep-sea coral 3 months following the closure of the Macondo well (Boehm and Carragher, 2012; White et al., 2012).

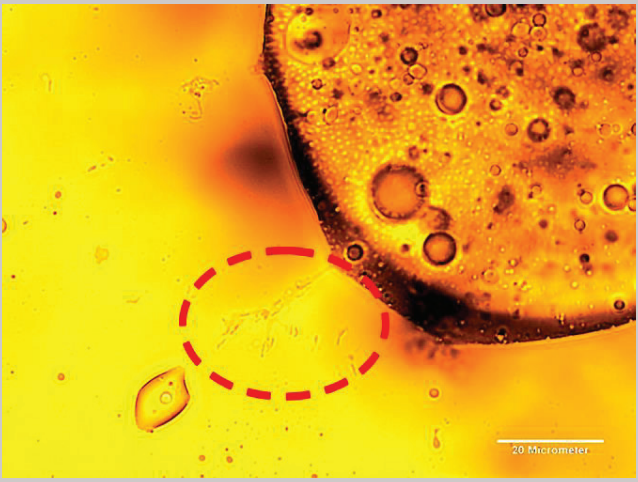

FIGURE A Bacteria from the deep intrusion layer attaching to a droplet of Macondo oil; the red circle indicates where the rod-shaped bacteria have attached to the droplet. SOURCE: © 2010 The Regents of the University of California, through the Lawrence Berkeley National Laboratory.

continued

BOX 2.2 Continued

Did SSDI enhance biodegradation of surfacing oil?

Based on the findings of Kujawinski et al. (2011), components of the dispersant dissolved into the deep intrusion layers while the oil droplets (depending on their size) rose through the water column, reaching the surface. The aqueous solubility of the nonionic surfactants may have allowed some components of the dispersant to reach the surface with the oil, consistent with on-scene reports that the behavior of the surface slick near the wellhead changed following the onset of SSDI. Based on the premise that surfacing droplets contained a fractionated subset of the applied formulation, some attenuated effect of SSDI is anticipated in the surface slicks, though detailed behavior is difficult to predict. Furthermore, SSDI-treated oil is expected to surface over a wider area than for untreated oil, with less thickness and at least somewhat less volume; hence, it may be subject to greater natural dispersion (Johansen et al., 2015), with the potential to stimulate biodegradation.

Was SSDI effective at facilitating biodegradation during DWH?

The situational complexities of DWH preclude a simple answer to this question. However, based on chemical and biological measurements, two key points emerge. First, the deep ocean microbial bloom response to DWH was significant and contributed to the fate of the discharged hydrocarbons trapped in the ocean's interior (Du and Kessler, 2012; Dubinsky et al., 2013; Hazen et al., 2010; Mason et al., 2012; Valentine et al., 2012). This was the case with and without SSDI (Dubinsky et al., 2013; Hazen et al., 2010). Second, because SSDI did not induce trapping of a large fraction of liquid hydrocarbon mass at depth (Gros et al., 2017; Ryerson et al., 2012), its effect on biodegradation in the deep ocean was limited to a small fraction of the total discharge, and primarily to the subset of compounds that are both soluble and volatile.

oil, and the time frame for development of a microbial community runs concurrent with the window for dispersant application. Microbial community development is itself a dynamic process that incorporates inherent properties of the microbes and oil with environmental variables and ecological feedbacks. Several key processes are considered below for their relevance to dispersant application.

Petroleum hydrocarbons provide carbon and energy substrate for the community of microbial consumers, but petroleum contains insufficient quantities of bioavailable nitrogen, phosphorous, or iron to support nutrient demand for growth. As a result, nutrient availability is key to the development of a petroleum-hydrocarbon-degrading community and, in turn, to the rate of petroleum hydrocarbon degradation. In this regard, the DWH spill provided a stark contrast to previous research on this topic because the surface waters in the vicinity of discharge were nutrient depleted. As would be predicted from this circumstance, biodegradation of floating oils was slow to occur (Edwards et al., 2011), and its cumulative effect on the chemical composition of floating oils was minimal (Ward et al., 2018b). Many previous studies included nutrient amendments (e.g., Hazen et al., 2010; Wardlaw et al., 2011); used nutrient-rich seawater (e.g., Brakstad et al., 2018b; McFarlin et al., 2014; Prince et al., 2013, 2016); or provided no information about nutrients (e.g., Wammer and Peters, 2005)—highlighting the need to rigorously consider nutrient availability specific to any discharge or biodegradation scenario. This line of reasoning further raises an important point with regard to dispersant application in low-nutrient waters: If biodegradation is limited by nutrient availability, then dispersion of oil is predicted to have little or no effect on the rate or extent of biodegradation.

Microbial communities are known to structure along the ocean's thermal gradients (Sunagawa et al., 2015; Swan et al., 2013), with a range of adaptations to cold water that include tolerance to cold temperature—psychrotolerance—and an absolute need for low temperature to support growth—psychrophily. Adaptation to cold temperature occurs among hydrocarbon degraders as evidenced from studies both in the polar regions (McFarlin et al., 2014) and in the deep ocean (Cao et al., 2014). Two key points about petroleum hydrocarbon degradation in cold environments are relevant to this report. First, some models (OSCAR[3]) assume exponential temperature dependence on reaction rates, commonly known as the Q10. This approach is potentially flawed, because the actual environmental rate is also dependent on the population size, which violates the assumptions that underlie the presumed exponential dependence (Bagi et al., 2013). Second, for the case of petroleum hydrocarbons discharged to or entering cold waters, the environmental factors structuring microbial response are expected to differ compared to warmer waters. Notably, growth rates are expected to be slower, though many cold water environments are rich in nutrients, and here nutrient limitation is less likely to occur.

Microbes can biodegrade petroleum hydrocarbons dissolved in the aqueous phase or present at the oil-water interface (CRRC, 2017), and physical access to oil is an important consideration for biodegradation. Several physical processes may influence microbial access to oil. Droplet size is an important consideration for biodegradation, and reduction in droplet size is the primary objective of dispersant application. Assuming no other limitation on microbial growth, increased surface area is expected to enable greater colonization of oil, which has been observed in laboratory studies (Brakstad et al., 2014, 2015; Ribicic et al., 2018) and is consistent with environmental observations (Bagby et al., 2017). Wax formation is also a relevant process that potentially links temperature, biodegradation, and dispersant efficacy (NRC, 2005). Biodegradation can enhance the overall wax content of the oil by depleting low molecular weight compounds, and hydrocarbon phase transformation to wax has recently been shown to suppress the biodegradation rates for a model hydrocarbon-degrading microbe (Lyu et al., 2018). Wax formation is also temperature and composition dependent, which opens the possibility that biodegradation, temperature change, and dispersant application could collectively modulate phase transition. During DWH, for example, wax formation could be inferred from imagery (Joye et al., 2011) and enrichment of high molecular weight alkanes (Bagby et al., 2017; Stout et al., 2016) but was never conclusively demonstrated in the deep ocean. Sediment deposition is also a relevant process that potentially links biodegradation and dispersant insomuch as dispersant application may affect the sedimentation of petroleum hydrocarbons by any of several mechanisms, as discussed in the section above regarding oil particle aggregates. When petroleum hydrocarbons are deposited on the deep seafloor (Stout et al., 2016; Valentine et al., 2014), biodegradation slows substantially (Bagby et al., 2017)—perhaps because of limitations to oxygen supply (Mason et al., 2014) or perhaps because of limited physical access to the oil.

The DWH spill provided impetus to study the interaction of microbial communities with dispersed oil in the context of deep ocean discharge and SSDI. Laboratory-based studies have considered both the rate and the extent of biodegradation as well as the dynamics of the microbial population (Bælum et al., 2012; Hu et al., 2017; Kleindienst et al., 2015b), while field studies have focused primarily on interpreting the observed patterns of chemical compounds and microbial communities in the deep ocean (Crespo-Medina et al., 2014; Dubinsky et al., 2013; Hazen et al., 2010; Kessler et al., 2011a; Lu et al., 2012; Mason et al., 2012; Rivers et al., 2013; Valentine et al., 2010). The environmental relevance of laboratory studies is confounded by the inherent limitations of study design. For example, Kleindienst et al. (2015b) and Hu et al. (2017) attempted to mimic in situ conditions but used a closed system approach for incubations exceeding 1 month duration, which excludes the many effects from mixing (e.g., dilution of hydrocarbon concentration and the introduction of nutrients, particles, microbial competitors, and predators). One key discrepancy between closed system experimentation and in situ conditions derives from the aqueous solubility

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[3] See https://www.sintef.no/en/software/oscar.

of surfactants used in most chemical dispersant formulations. Compounds such as DOSS are aqueous soluble and are expected to gradually dissolve from suspended droplets and partition to the large volume of the ocean (Kujawinski et al., 2011). But in closed system experiments (Hu et al., 2017; Kleindienst et al., 2015b), dispersant remains with the oil, deviating substantially from in situ conditions and potentially explaining why observed taxon abundance differs from field observations (Delmont and Eren, 2017) and from parallel experimental treatments lacking dispersant (Kleindienst et al., 2015b). For these reasons, the extrapolation of findings from these laboratory studies to in situ behavior is avoided here. A second key discrepancy between closed system experimentation and in situ conditions derives from sample treatment. For example, Hu et al. (2017) pretreated samples with oil weeks before initiating incubations, which nullifies claims about initial population growth rates, succession patterns, and reaction rates.

Field studies conducted following DWH (Crespo-Medina et al., 2014; Dubinsky et al., 2013; Hazen et al., 2010; Kessler et al., 2011a; Kleindienst et al., 2015a; Lu et al., 2012; Mason et al., 2012; Rivers et al., 2013; Valentine et al., 2010) have provided insight as to the identities and mechanistic pathways for hydrocarbon-utilizing bacteria in the deep ocean. However, these studies also face limitations because each provides only snapshots of a complex and changing landscape, and in aggregate they suggest as-yet undiscovered processes or methodological inconsistencies. While deep ocean microbial communities clearly bloom in response to input of petroleum with or without SSDI, the exact sequencing of substrate consumption, the dynamic factors that structure the microbial response, and the in situ impact(s) of SSDI are viable research questions.

TRANSPORT PROCESSES

Subsurface Transport

Importance of Droplet Size

Oil fate and transport in the water column are largely determined by the size distribution of oil droplets. On the surface, oil droplets form when turbulence generated by waves and currents acts on a surface slick and drives oil into the water column. The depth of penetration of oil droplets into the water column and the time it takes for the droplets to rise back to the surface depend on the oil droplet size (as well as the oil density, presence of currents, and turbulence). For droplets smaller than ~70 µm, there is some evidence suggesting that, effectively, they will remain permanently suspended in the water column (Lunel et al., 1995). In the event of a subsurface deepwater release, such as a well blowout, droplets formed at the point of release will rise through the water column as a function of their size. Larger diameter droplets rise more quickly than do smaller diameter droplets, as described by the generalized Stokes' Law for the drag force on a spherical object (e.g., Zheng and Yapa, 2000). The importance of droplet size on the rise time in a deepwater spill is illustrated in Figure 2.10, where the droplet rise was modeled using the generalized Stokes' Law. Figure 2.10 indicates substantial delays in oil surfacing time for smaller droplet sizes. Very small droplets and dissolved oil lack buoyancy to reach the surface, and they can become trapped in deep intrusion layers (see Figure 2.10).

As discussed earlier in the chapter, dissolution of soluble components increases with time spent in the water column, such that the longer a droplet is submerged, the more dissolution will occur. In surface waters, atmospheric exposure results in volatilization of the lower molecular weight components of the oil reducing the extent of its dissolution. In a deepwater spill, smaller oil droplets with a larger surface area will lose more of their soluble components and hence release fewer volatiles to the atmosphere when they reach the surface. This is a major consideration for response operations because exposure to VOCs is a key health concern for the response workers

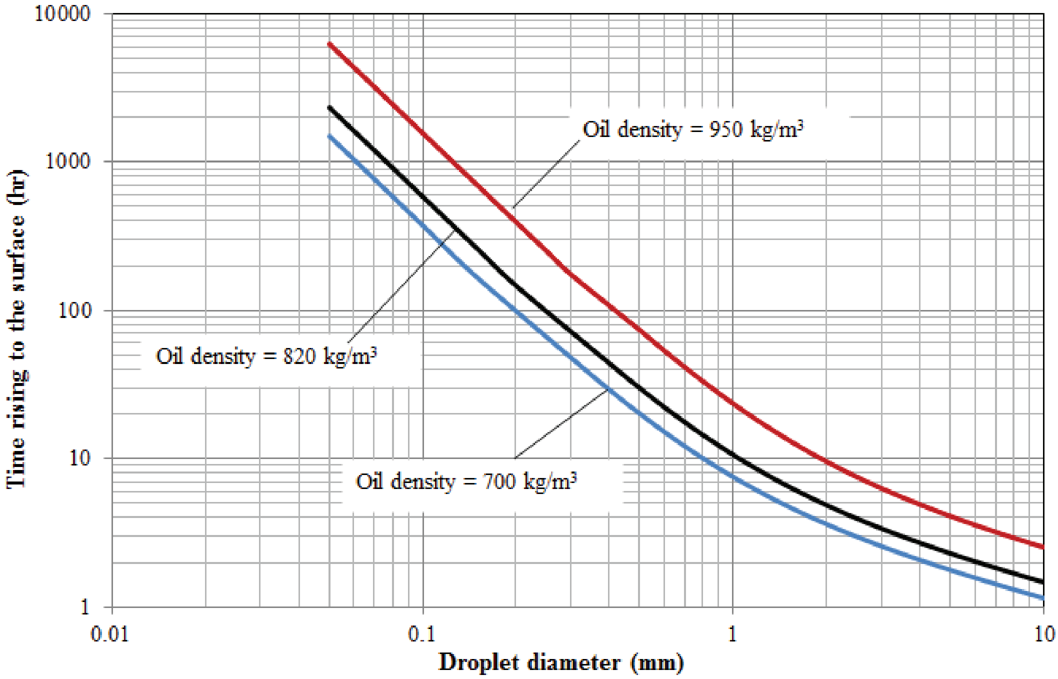

FIGURE 2.10 Rise time for droplets of various sizes and densities to reach the water surface from a depth of 1,500 m. These are for dead oil where the density of the droplets does not change over time. Note also that droplets with a diameter of less than 1.0 mm take significantly longer to reach the surface. For example, for oil density of 820 kg/m^3, a 1-mm droplet will surface in about 10 hours while a 0.5-mm droplet will take about 30 hours. SOURCE: Committee-generated based on the general equation for droplet rise in quiescent water.

in the area of the spill. The increased surface area and time in the water column associated with smaller droplets may also potentially promote biodegradation depending on the specific conditions and extent of exposure; however, limited empirical studies have directly tested this hypothesis for a response-relevant scenario, preventing generalized conclusions on this point.

From an ecological perspective, enhanced dissolution, enhanced biodegradation, and entrainment of small oil droplets reduces the amount of oil that reaches the surface, potentially reducing the impact on organisms that live at or near the surface, such as air-breathing turtles, marine mammals, and seabirds. Furthermore, a reduction in the amount of oil at the surface may lower the amount of oil reaching sensitive shoreline habitats, such as marshes (Boehm et al., 1987). However, greater concentrations of oil and oil components, including BTEX compounds and PAHs, sequestered in the deep sea may have serious implications for benthic, mesopelagic, and potentially epi-pelagic resources (Romero et al., 2018), including deep-diving marine mammals foraging at depth. Because the primary objective of dispersants is to promote the formation of smaller droplets, understanding the implications of varying droplet size distributions is critical to making decisions and predictions regarding dispersant use. Chapter 6 provides some insights into this complex set of response trade-offs using integrated models.

Droplet Models

Due to disparity of scale in droplet formation processes, potentially high pressure, and other factors, no experimental system or model will perfectly replicate conditions in the field associated with an actual spill. Instead, experiments and models provide a way for scientists to understand how different components and processes may influence the size, distribution, and behavior of droplets. For example, experimental systems can examine the effect of different oil types, different proportions of methane, the effect of different dispersants, and DORs. Similarly, models can be used to explore different spill scenarios by varying parameters—such as flow rate, depth, or DOR—that are described by the models. Experiments can be designed to test how well models perform at different scales. Because experiments and models are simplifications of actual conditions, however, their predictive power rests on their ability to replicate the most impactful of the processes. For any particular spill, unforeseen conditions may impact droplet size formation and complicate reconstruction of the actual conditions, such as ancillary small-aperture fissures or changes in pressure, fraction of methane, and others.

Understanding the dynamics associated with droplet formation and transport is important to forecasting and preparing for the impacts of an oil spill. In a deepwater spill, droplets will diffuse in three dimensions as they rise through the water column. Models for droplet formation and transport have been developed to help understand the factors that affect these processes and improve capabilities to forecast the fate of spilled oil. The focus of these models has been on processes, including turbulence produced by the discharge as well as physicochemical properties of the oil, water, and dispersant (i.e., IFT and viscosity). Several such models are discussed below, while surface droplet formation models are discussed later in this chapter.

The basic tenet of droplet formation is captured by the Weber number (We; Hinze, 1955), which represents the ratio of destructive forces due to turbulence to resisting forces due to surface tension. Amendments to this approach have been made to account for the resisting role of oil viscosity, which resulted in the introduction of a dimensionless viscosity number (Calabrese et al., 1986; Hinze, 1955; Wang and Calabrese, 1986). Johansen et al. (2013) used this concept, developed for oil dispersion in reactors at steady-state, and applied it to the droplet formation from jets. Their approach became known as an "equilibrium" model, and a similar model was adopted by RPS ASA (Li et al., 2017c). These models predict the median droplet size (d_{50}) and specify a spread coefficient (width parameter) of the droplet size distribution (DSD), either as log-normal (LN) or Rosin-Rammler. The d_{50} is expressed in terms of nondimensional numbers that include a We and either a viscosity number (Vi; Johansen et al., 2013) or an Ohnesorge number (Oh; Li et al., 2017c) to account for the combined resistance of oil-water interfacial tension and oil viscosity to droplet breakup. All quantities for the prediction of the DSD were evaluated based on the conditions at the source (e.g., velocity and orifice diameter), and while the models are physically based, they involve calibration coefficients. Both models account for oil constriction due the flow of gas from the orifice, but neither accounts for the interaction between oil droplets and gas bubbles. Nor are the models capable of predicting gas bubble size, at least not with the existing calibration coefficients. Both models can predict DSDs where some of the droplet sizes exceed the maximum stable droplet size. To resolve this, they redistribute those droplets using heuristic approaches. It should also be pointed out that the RPS ASA's model uses oil properties at the surface; thus, it does not account for the change in oil physical properties at depth in the presence of natural gas (e.g., larger interfacial tension, lower viscosity and density).

Paris et al. (2012) also used the equilibrium-model approach and predicted the d_{50} for the DWH in the absence of dispersant to be less than 100 µm. Adams et al. (2013) argued that the constant of proportionality used by Paris et al. (2012) was 100-fold smaller than that used by Johansen et al. (2013), likely because the Paris et al. (2012) model was based on droplets observed in a stirred reactor as opposed to droplets formed by a jet of oil. Further modeling done by Socolofsky and Gros (see Appendix E), and described in Chapter 6, suggests that the d_{50} used by Paris et al. (2012) for the DWH simulations were smaller than those generated from most ambient pressure jet-based experiments.

In contrast with the equilibrium models described above, "population" models are numerical models that solve for the hydrodynamics at each distance from the orifice and allow for the evolution of the DSD. Examples are VDROP-J (Zhao et al., 2014b) and Oildroplets (Nissanka and Yapa, 2016). The models incorporate the local physics (mixing energy, droplet density) to track the evolution of each droplet size and gas bubble size and simulate droplet breakup and coalescence as a function of distance along the plume trajectory. Unlike equilibrium models, this type of model can compute spatially varying DSDs. The models assume a continuous discharge at statistical steady-state and move fluids downstream of the orifice while accounting for water entrainment and the change of jet hydrodynamics with distance from the orifice. Both models include a calibration coefficient that depends on the jet hydrodynamics.

These models address how turbulence induces droplet breakup (i.e., dynamic breakup), but they do not consider an additional breakup mechanisms when dispersant is present known as tip streaming (Gopalan and Katz, 2010). Tip streaming results from capillary instability on the droplet surface caused by the migration of surfactants on the droplet surface driven by water vorticity (Tseng and Prosperetti, 2015); the surfactant concentration on the oil droplet reaches maximum values at locations where the water vorticity vanishes. Tip streaming has been observed to cause dispersant-coated oil droplets—with initial diameters of several mm—to form much smaller microdroplets over a time scale of several minutes (Nagamine, 2014). Zhao et al. (2017b) measured DSDs from a horizontal jet of oil in seawater using a laser light scattering instrument (i.e., Sequoia's Laser In-Situ Scattering and Transmissometry [LISST] instrument). The unimodal DSD was measured at d_{50} = 114 mm without dispersant, while with dispersant premixed at a DOR of 1:20, the distribution was strongly bimodal, with d_{50} = 5.9 mm and a plurality of the droplets having diameters less than 2.7 mm. The bimodal distribution with this range in the presence of dispersant has been observed in the literature of oil release from jets (Gopolan and Katz, 2010; Murphy et al., 2016) and from oil spills on the water surface (Li et al., 2009b). Zhao et al. (2017b) inferred that tip streaming occurred in their experiment, and they introduced into VDROP-J a mechanism to account for tip streaming. With a calibrated rate constant, they were able to reproduce numerically the observed bimodal DSD.

The presence of microdroplets in the intrusion layer at DWH was verified by observations made with a holographic camera system—holocam (White et al., 2016)—and other systems (Li et al., 2015), but they show very low concentrations. Microdroplets were formed in both the presence and the absence of dispersants premixed with oil. As the holocam measurement only captures part of one side in the intrusion layer, it is difficult to extrapolate to the full volume. Microdroplets were entrained in the subsurface plume prior to the application of SSDI, indicating that some process other than SSDI was responsible. This may have included escaping small droplets from small fissures in the broken riser pipe or explosive oil releases from the large end of the open riser due to the large pressure drop associated with release of oil and gas into the environment. However, the microdroplets do not appear to have been sufficiently abundant to account for a large fraction of the oil mass (Gros et al., 2017).

There are several physical processes that could potentially influence droplet sizes in certain release scenarios, and which are not considered by either equilibrium models or the population models. Those processes include oil droplet degassing, and pressure drop and churn flow in the blowout preventer (BOP). The first process is the degassing of saturated oil droplets. Using a counterflow apparatus, Pesch et al. (2017) showed that, if the rate of degasification exceeds the rate of gas dissolution, the degassed bubbles could cling to the oil droplets, thus reducing the time they take to reach the surface relative to similar-size purely liquid droplets.

A second process derives from observations from the DWH spill that there was a substantial pressure drop between the reservoir and the end of the BOP-riser where the oil and gas discharged to the ambient ocean (Aliseda et al., 2010; Wereley, 2010). The pressure gradient was no doubt complicated in the BOP-riser by the BOP geometry, the broken BOP rams, and other debris. A pressure gradient with live oil, if steep enough, could conceivably cause smaller droplets than are calculated in present versions of the equilibrium and population models.

Finally, both the equilibrium models and the population models assume that the live oil exits the orifice uniformly. An argument has been made (Boufadel et al., 2018b) that churn flow could occur, which would also lead to smaller droplet sizes. However, their analysis was also based on the assumption of a relatively unobstructed riser pipe.

The manner in which various mechanisms involved in oil and gas fate and input parameters are incorporated may contribute to the differences observed in model results. The occurrence of these processes in the DWH spill is contentious (Malone et al., 2018; Paris et al., 2012; Pesch et al., 2018), and these processes (degassing, pressure drop, and churn flow) deserve further study.

Observations of Droplets in the Laboratory and Field

Since DWH, measurements of droplet and bubble formation using different fluid mixtures in blowout-like conditions at different depths and flow rates have been conducted by various groups. With respect to dispersant use, these studies suggest that SSDI with a DOR of 1:50-1:100 reduces the IFT of oil by roughly two orders of magnitude for the lighter oils that characterize high-volume blowouts. This corresponds to roughly one order of magnitude reduction in the d_{50} (Brandvik et al., 2013, 2014a, 2017b, 2018, 2019a,b). In addition, SSDI effectiveness is demonstrated to be fairly insensitive to the injection method at laboratory scales (release orifice of 1.5 mm), and even a wand placed up to 6 diameters away from the discharge orifice worked well in dispersing oil. No evidence was found of partially treated oil as suggested by Spaulding et al. (2015), even when the DOR was dropped to less than 1:250 (Brandvik et al., 2014a, 2018). However, the extent to which these findings may be valid at a full-scale field blowout remains uncertain. Brandvik et al. (2014b) found that dispersant effectiveness decreases as oil temperature rises, but this impact could be largely countered by increasing the DOR from 1:100 to 1:50. They also found that dispersants were not as effective on waxy oils compared to lighter oils. Finally, this study suggests that the solvent component of Corexit® may not contribute to its effectiveness when used in SSDI. This finding, coupled with the temperature sensitivity noted above, suggests that further research could result in a more optimized dispersant for SSDI use.

Direct measurement of droplet/bubble sizes in the lab or field has been a challenge. The LISST instrument cannot measure droplet sizes above 500 mm, cannot distinguish between oil droplets and gas bubbles, and does not work at high concentrations of droplets/bubbles. Recent advances in instrumentation have produced the Silhouette camera (SilCam) (Davies et al., 2017a) and the Shadowgraph camera (developed by the consortium CARTHE), which appears to overcome the first two limitations and push the concentration threshold considerably higher than the LISST's. Holographic imaging has also been used (Murphy et al., 2016a; White et al., 2016).

In experimental systems, the problem with measuring droplet size at high oil concentrations can also be resolved by using a horizontal discharge or by applying horizontal currents, either of which will dilute the droplet concentration. At the same time, these approaches risk biasing results due to droplet fractionation.

Observations of the physicochemical characteristics of oil that reached the surface following the DWH spill have been used to estimate the rise velocity of oil droplets and droplet size distribution (Ryerson et al., 2011, 2012). This team observed that large volumes of oil surfaced within 3-10 hours of wellhead discharge and surfaced within 2 km of the wellhead. Recent modeling by Gros et al. (2017) validated with field data of oil composition in different compartments, inferred that the DSD with dispersant application in the DWH spill had a d_{50} of around 1 millimeter, which falls within the range of 0.5 to 5 mm estimated by Ryerson et al. (2012).

Model Validation

The committee members could not reach consensus on the merits of including a model-data comparison. Some committee members had concerns about the lack of peer-reviewed, published analyses of the datasets, with some members also concerned about the representativeness of the experimental data, in particular the issue of droplet fractionation in horizontally directed droplet plumes. Two committee members disagreed, however, arguing that model-data comparisons were vital to understanding model uncertainty, and hence addressing the sixth task of the committee's Statement of Task. Their opposing view and analysis are contained in Appendix D.

Model Predictions at Field Scale

The values of d_{50} predicted by SINTEF's model, RPS ASA's[4] model, VDROP-J, and Paris et al. (2012) models when applied to the DWH spill are shown in Table 2.1. The most relevant row is the 1:250 DOR that corresponds to the average dispersant injected during this time period (Spaulding et al., 2017). VDROP-J and SINTEF calculate a droplet size of 1.3 to 1.8 mm. Gros et al. (2017) show that droplets of this size can reasonably replicate the observations. The droplet sizes produced by the Paris et al. (2012) model are substantially smaller.

For RPS ASA's model, two columns are shown. The first from Spaulding et al. (2017) shows two d_{50}s corresponding to the two peaks assumed in their DSD. Spaulding et al. (2017) suggest that the oil was only partially treated by dispersant based on video taken at the wellhead, in which bands of whitish and darkish oil imply that some oil was dispersed and some was not. Their dual-peaked DSD model reasonably reproduces the subsurface observations during the periods examined, but they did not look at the surfacing times estimated by Ryerson et al. (2012). Further work done by Socolofsky and Gros (see Appendix E) compares the dual-peaked DSD to the dataset assembled by Gros et al. (2017) and shows that it does not fit observations nearly as well as the single-peaked distribution from the VDROP-J or SINTEF models.

Table 2.1 also includes a column showing the droplet size predicted by RPS ASA's model assuming 100% mixing of the dispersant (fully mixed). In general, these numbers are within about two times of SINTEF's model numbers and VDROP-J numbers.

Nearfield Plume Dynamics

Gas bubbles and oil droplets released from a blowout create a buoyant multiphase plume. The plume entrains ambient seawater, elevating it within the water column. As the plume rises, the gas bubbles and smaller molecules of the oil droplets dissolve into the entrained seawater. This decreases plume buoyancy and reduces bubble and droplet diameters, thereby affecting their rise velocity and the concentration of dissolved hydrocarbons in the plume. Eventually, ambient density stratification and currents cause the entrained seawater to detrain from the plume, forming lateral intrusion layers of enhanced hydrocarbon content, as were observed more than 100 km downstream of the DWH blowout (Du and Kessler, 2012; Kessler et al., 2011a). The plume width and intrusion layer thickness span scale up to a few hundred meters (see Figure 2.3), much smaller than the resolution of ocean circulation models; hence, these features are simulated using sub-models specifically designed to capture fine-scale dynamics. Because of the plume effect, droplets rise more rapidly below the intrusion layer than they do above it, where they rise as individual droplets.

Buoyant multiphase plumes in stratification and crossflow have been studied in the laboratory and the DeepSpill field experiment (Johansen et al., 2003). Key parameters include w_r = bubble/

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[4] For the purpose of clarity in this discussion, the committee uses "RPS ASA's model" here and henceforth to refer to the model initially developed by Li et al. (2017c) and subsequent modifications of that model.

TABLE 2.1 The d_{50} Predicted by Four Models (SINTEF's model; RPS ASA's model; VDROP-J; and the Paris et al. [2012] model) for Both Untreated Oil and Oil Treated with 1:250 and 1:100 DOR in a Scenario That Simulates the DWH Spill

DOR	SINTEF's Model[a] (μm)	RPS ASA's Model[b] Partially Mixed (μm)	RPS ASA's Model[c] Fully Mixed (μm)	VDROP-J[d] (μm)	Paris et al., 2012 (μm)
0	5,800	2,600	10,200	4,200	190
1:250	1,800	100/2,600	3,400	1,300	70
1:100	530	200/2,600	740	140	10

[a] Calculated using ρ_o = 707kg/m^3, μ = 0.74cp, GOR = 0.41 at seabed, σ = 24.5 cp (DOR = 0), σ = 4.54 mN/m (1:250), σ = 0.24 mN/m (1:100). For diameters > the stable droplet size, sets d95 = max stable droplet size.

[b] These are approximate peaks taken from Figure 9 of Spaulding et al. (2017). The 1:250 DOR case in the table comes from their "Best Estimate," while the 1:100 comes from their "high dispersant" case. The dual peaks in the DSD arise because they have assumed only partial mixing of the dispersant. See further discussion in the text.

[c] These are estimates assuming that the dispersant is 100% mixed and uses oil characteristics at the surface as per Li et al. (2017c). ρ_o = 862 kg/m3, μ = 0.74 cp, GOR = 0.4 at seabed, σ = 24.5 mN/m (DOR = 0), σ = 4.54 mN/m (1:250), σ = 0.24 mN/m (1:100).

[d] From Gros et al., 2017.

droplet rise velocity; B = kinematic buoyancy flux of dispersed-phase particles; N = buoyancy frequency of ambient stratification; and u_a = ambient current velocity (Socolofsky and Adams, 2002, 2005). $(BN)^{1/4}$ is a characteristic velocity and $B^{1/4}/N^{3/4}$ and B/w_r^3 are characteristic lengths of a multiphase plume (Bombardelli et al., 2007). Combinations of these parameters have been used to predict plume characteristics.

Although self-similarity is not strictly valid for multiphase plumes, integral models based on the entrainment hypothesis have been successfully applied to predict multiphase plume dynamics (Milgram, 1983). Major blowout simulation models are DeepBlow (Johansen, 2003), the Clarkson Deep Oil and Gas (CDOG) model (Zheng and Yapa, 2002), and the Texas A&M modeling system (Texas A&M Oilspill Calculator [TAMOC]; Dissanayake et al., 2018). These models have been carefully validated and can simulate some fate processes. Disadvantages are that they cannot resolve unsteady flow features or the complex processes of detrainment, intrusion formation, and weak plume dynamics above the detrainment point.

Recently, large-eddy simulation models have been developed to treat complex oil and/or gas plumes in stably stratified conditions (Fabregat et al., 2015, 2016; Fraga et al., 2016; Yang et al., 2016a). These models do not rely on self-similarity. Instead, they are fully three-dimensional and are able to directly resolve large- and intermediate-scale turbulent motions, relying on turbulence closure models for the effects of subgrid-scale features. Yang et al. (2016a) used their large-eddy simulation model to assess the flux parameterizations typically used in integral plume models, and they proposed a new continuous peeling model for double-plume integral models with a more self-consistent performance than previous models.

Intrusion Layer Formation

The previous discussion described nearfield plume dynamics, showing how buoyant oil and gas released at the bottom of a stratified ocean can become trapped in layers, centered on the level of neutral buoyancy of the entrained seawater. It is of interest to know whether oil droplets also

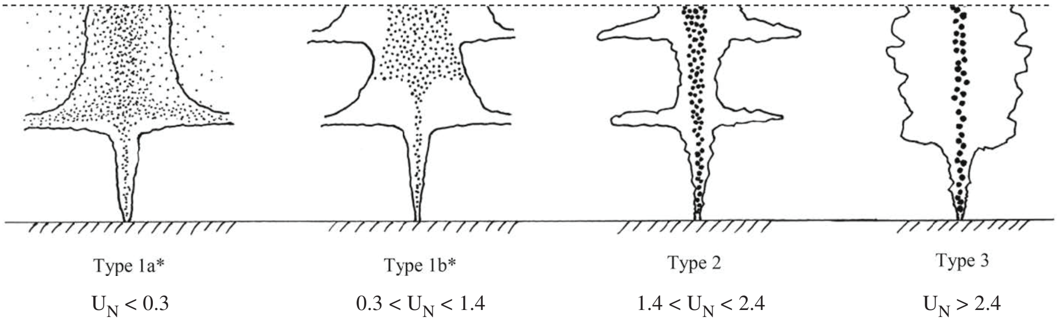

FIGURE 2.11 Plume classification scheme proposed by Chan et al. (2015). SOURCE: Chan et al., 2015.

become trapped. Experimental studies suggest the classification shown in Figure 2.11 (Chan et al., 2015), indicating that as the characteristic velocity $U_N = w_r/(BN)^{1/4}$ decreases, droplets become more effective in pumping ambient water upward to one or more intrusion layers, and there is greater tendency for droplets to detrain and enter the intrusion themselves. Chan et al. (2015) found a threshold value of $U_N = 0.2$ to 0.4 below which droplets intrude. They also derived theoretically and confirmed experimentally a relationship for the distance *sr* that a droplet travels within the first intrusion layer before escaping, given by

$$\sigma_r = \sqrt{\frac{0.9-0.38\left(U_N\right)^{0.24}}{\pi}\frac{B^{3/8}}{N^{5/8}w_r^{1/2}}}. \qquad (1)$$

Additional experiments have been conducted to establish similar threshold values of U_N and lateral transport distances for oil discharging into a mild current (Wang and Adams, 2016).

Using Equation 1 for an oil with a density of 0.85 g/cm^3:

- droplets with a diameter of 2 to 20 mm, typical of those expected for untreated oil at DWH (Testa et al., 2016), would have been transported 50-100 m radially within the intrusion layer;
- droplets with a diameter of 0.2 to 2 mm, typical of those for dispersant treated oil not experiencing any tip-streaming breakup (Zhao et al., 2015), would have traveled 100-500 m laterally; and
- droplets with a diameter of 0.02 to 0.2 mm, typical of those expected at DWH for dispersant treated oil experiencing significant tip streaming or rapid pressure drops following release, could theoretically have been transported 3-20 km before rising out of the intrusion layer.

These transport distances are in general agreement with predictions for similar droplet sizes in farfield transport models (North et al., 2015; Paris et al., 2012).

In an ambient current, the rising plume is pushed downstream and forms an intrusion layer composed of a pair of counter-rotating vortices (Murphy et al., 2016a; Socolofsky and Adams, 2002). Droplets and bubbles rise out of the intrusion in accordance with their size. The intrusion thickness also reflects the droplet size, with larger droplets producing a thicker intrusion due to their faster rise velocity (Murphy et al., 2016a). Plumes have been modeled for both quiescent and flowing environments (e.g., Dissanayake et al., 2018).

Surface Transport

Oil Dispersion

The formation of oil droplets in water is commonly referred to as "dispersion" in the oil literature, and it is distinct from the traditional definition of dispersion in fluid mechanics introduced by Taylor (1953), which means the spreading of solute in a solvent due to the spatial variation of velocity. Oil dispersion forms as a result of "destructive" forces due to water hydrodynamics (e.g., turbulence) and "resisting" forces due to oil-water IFT and the oil viscosity (Grace, 1982; Hinze, 1955).

Models of Droplet Breakup Under Surface Slicks

Oil that is spilled on the surface is also subject to dispersion caused by breaking waves. Though this occurs naturally, it can be enhanced by surface application of dispersants. The dispersion causes the oil to break into small droplets, which can be entrained below the surface by waves, turbulence, and Langmuir circulation. Their depth and the persistence of the dispersion in the water column depend on droplet size, where smaller droplets are less buoyant and tend to entrain deeper into the water column and persist there longer. Droplets smaller than 70 μm have been observed to remain permanently suspended in the water column (Lunel et al., 1995).

Until recently, most models of surface oil dispersion have relied on the study by Delvigne and Sweeney (1988, DS model), which was summarized in the NRC (2005) study. In the DS model, the number of oil droplets for each size is a power law of that size, namely:

$$N \sim d^{-a} \tag{2}$$

where "a" is a constant around 2.3. The committee notes that Equation 2 describes a DSD based on the number of droplets, rather than mass, as described earlier in connection with subsurface droplet size distributions. The simplicity of Equation 2, and the fact that the model provides a way for entraining droplets into the water column, has contributed to the popularity of the DS model. A group of researchers at the Department of Fisheries and Oceans (DFO; also known as Fisheries and Oceans Canada) reported a series of dispersion experiments in the wave tank at the Bedford Institute of Oceanography (Li et al., 2008a,b, 2009a,b,c, 2010). They found the total oil concentration to be related to the energy dissipation rate through the equations $c \sim e^{0.32}$ and $c \sim e^{0.43}$ for oils without and with dispersant, respectively. They observed the droplet size mass distribution to be log-normal in the absence of dispersant and bimodal when dispersants were used. In the latter case, they found one peak to be below 10 μm and another at 100 μm or larger, depending on the oil and mixing energy. Attempts at modeling the DSD of the DFO data were conducted by Boufadel et al. (2008) and Chen et al. (2009). Zhao et al. (2014b) used the VDROP-J model to predict the DSD under hypothetical breaking waves at sea. They accounted indirectly for the entrainment by removing droplets smaller than 100 μm from the slick. However, the approach is very demanding computationally and requires detailed data for calibration, which are not available for different wave configurations.

A limitation of the DS model is that, while it accounts for viscosity, it does not consider IFT. Indeed, the range of IFT used by DS was narrow from 18 to 30 mN/m, which is representative of untreated oil but not chemically dispersed oil. More recently, Zeinstra-Helfrich et al. (2017) revisited the DS equations, introduced the impact of IFT, and proposed a dispersibility factor to determine when dispersants should be used. Their approach assumes that the DSD follows a log-normal mass distribution, which agrees with observations in the absence of dispersant.

Johansen et al. (2015) developed a semiempirical model for oil DSD generated by single breaking wave events based on the theoretical framework of the Weber and viscosity numbers

(Calabrese et al., 1986; Hinze, 1955) adopted in Johansen et al. (2013) for jets. The model has several improvements over that of Delvigne and Sweeney (1988). In particular, the roles of both IFT and viscosity are physically represented, and the results are expressed in dimensionless form. In addition, the underlying lab experiments were shown to support a log-normal relationship for DSD. Like Johansen et al. (2013), the model expresses droplet diameter—in this case, normalized by the slick thickness—as a function of two nondimensional groups: We and the Reynolds number (Re). The velocity in the two numbers is given by U = sqrt(gH), where H is the wave height. An experimental full-scale oil spill, conducted offshore Norway in July 1982, was used to validate the model. However, the range of independent variables that were varied in the laboratory was limited, making it tenuous to extrapolate the predictions to the field.

RPS ASA's model used a similar approach as did Johansen et al. (2015) to derive a generalized droplet model that would apply to natural dispersion at the surface as well as the previously described dynamic breakup due to a deepwater[5] blowout. Their formulation relates normalized droplet size to We and Oh and was calibrated to droplet data collected in a wave tank for a broad range of viscosity and IFT. They used various DORs for the latter. Noting that Li's Oh can be related to Johansen's Re and Vi, both models can express normalized droplet size as a function of two dimensionless variables, say We and Re.

As with subsurface droplets treated with dispersants (discussed earlier), surface oil treated with dispersants can break down into micron (and smaller) sized droplets due to tip streaming. In this process, dispersant migrates on the oil droplets to form a cone where the oil and dispersant leave the droplets and form microdroplets (Gopalan and Katz, 2010; Tseng and Prosperetti, 2015). The presence of microdroplets has been inferred by Zhao et al. (2017b). However, turbulence-based models—such as presented by Johansen et al. (2013), Zhao et al. (2014a), and Li et al. (2017c, RPS ASA's model)—cannot predict microdroplets. This fact was noted by Zhao et al. (2017b), and they proposed for this purpose a formulation for predicting tip streaming based on the surfactant concentration and the droplet Re. Due to their small size, the microdroplets are likely to be volatilized and thus have potential adverse implications on air quality (Sampath et al., 2017).

The spreading of oil on calm seas has been well predicted by the works of Fay (1969) and Hoult (1972), who used dimensional analysis to obtain order-of-magnitude type equations. At first, the oil spread due to gravity because oil rises to the top of the water surface and then it spreads because of the IFT between oil and water. They also argued that in the initial phase, spreading is impeded by inertia of the water, with water viscosity becoming the main resisting force after the initial phase. Their approach forms the basis of most oil spill models. However, the assumption of an infinitesimally thick oil slick floating on a stagnant water column does not apply well at sea due to the presence of wind, currents, and waves. For example, Lehr et al. (1984) conducted experiments and provided a model favoring the elongation of the oil with the direction of the wind. This results in a spill shaped as an ellipse with the long axis aligned with the wind direction.

The traditional approach for modeling an oil spill on the water surface assumes that the slick consists of many Lagrangian elements (sometimes called spillets), with each getting displaced by advection (due to currents), Stokes drift of waves (in the propagation sense of waves), wind (fraction of the wind speed), and turbulence (Boufadel et al., 2014; MacFadyen et al., 2011). The propagation speed of oil due to wind is typically taken as a fraction of the wind speed (obtained at 10 m above the water), and the fraction varies between 1% and 6% (ASCE Task Committee, 1996). Although the Stokes drift depends on wave properties, it is also taken for simplicity as a

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[5] The committee recognizes there are varying definitions for the terms "deep water" or "deep-water," which largely depend on the context of their use; however, for the purposes of this report, the committee generally considers "deep water" to be approximately 500 m or greater.

fraction of the wind speed, typically a few percent. The spread of oil spillets on the water surface is assumed to occur by diffusion, typically using a random walk process with a select turbulent diffusion coefficient. For the DWH, the coefficient was taken to be approximately 10 m^2/s in various studies (Barker, 2011; Boufadel et al., 2014).

These approaches are expedient but could fail in some cases. In particular, they do not account for convergence of ocean currents as revealed by D'Asaro et al. (2018), whereby drifters initially separated by 10 km converge within hours to within 10 m from each other. In addition, they do not account for the formation of windrows due to Langmuir cells (Golshan et al., 2017; Langmuir, 1938; Leibovich, 1980).

Entrainment

The vertical transport of oil droplets due to waves was first investigated experimentally and numerically (using an Eulerian approach) by Elliott et al. (1986), who noted also the formation of a comet-shape oil plume. They also reported the relative absence of oil droplets smaller than 70 μm from the surface layer. Various investigators found that "particles" released at the water surface tend to propagate downward. However, the downward migration is usually much slower than the horizontal migration. For example, a field study by French-McCay et al. (2008) found that the vertical diffusion coefficient is around 10 cm^2/s, while the horizontal diffusion coefficient is on the order of m^2/s. Attempts to understand the downward movement were conducted by Boufadel et al. (2006, 2007), who surmised that it is due to the orbital motion of waves combined with turbulent diffusion. They assumed second-order regular waves and investigated the impact of buoyancy and vertical diffusion on the migration of oil droplets released at the water surface. They noted that after 1 hour, the centroid of plumes of droplets of a given size stabilized at a depth directly related to the buoyancy (the larger the buoyancy, the smaller the depth). The exception was for the neutrally buoyant droplets that continued to propagate downward. A recent work by Geng et al. (2016) extended the work to irregular waves (Kitaigordskii et al., 1983) and found similar general conclusions.

Existing approaches for the displacement of oil droplets tend either to ignore the vertical profile of the vertical eddy diffusivity or to neglect it during simulations. The eddy diffusivity is expected to be small at the water surface, to increase with depth until reaching a maximum, and subsequently to decrease slowly with depth. However, most studies assume a uniform eddy viscosity with depth, which is contrary to the physics (Boufadel et al., 2018a; Marusic et al., 2013; Townsend, 1980). Studies by Visser (e.g., 1997) demonstrated that neglecting the viscosity gradient would erroneously accumulate particles at the water surface, a finding that was confirmed recently by Boufadel et al. (2018a). A recent numerical study using a Reynolds Average Navier Stokes model predicted that oil droplets tend to persist longer in the high-viscosity region (Golshan et al., 2018).

Existing approaches that rely on random walk for displacing oil droplets have come under scrutiny through a series of theoretical works (Eames, 2008; Santamaria et al., 2013) due to the neglect of the droplet inertia. These works did not account for turbulence, but they demonstrated that using the standard particle tracking approach would underestimate the rise rate of oil droplets due to the droplet inertia. In the presence of turbulence, studies found that droplets can rise three times faster than at the speed given by Stokes' Law (in quiescent water) (Friedman and Katz, 2002), which is through a mechanism known as trajectory biasing. However, this seems to apply to droplets that are larger than 500 μm.

Transport in the Water Column

Effect of Oil Droplet and Gas Bubble (Impact of Shapes)

With regard to blowouts, the above discussion has addressed the formation of oil droplets and gas bubbles and how these buoyant fluids interact in the nearfield with local ocean currents and stratification to form a plume and intrusion layers. In the farfield, mixing of oil droplets and dissolved hydrocarbons is considered passive, and Lagrangian stochastic models can be used to simulate subsequent fate and transport (North et al., 2015; Paris et al., 2012), especially when focus is on the large scale.

The locations, flow rates, and composition of oil droplets leaving the intrusion layers become initial conditions for the farfield transport models. These inputs can be obtained from integral or large-eddy simulation models of the nearfield, as discussed previously, or from correlation equations, as reported in Socolofsky et al. (2011). In the Lagrangian stochastic models, particles sizes are typically selected from the DSD at the end of the nearfield, either by binning the data (North et al., 2015) or by a random number generator matched to the DSD probability function (Paris et al., 2012).

The boundary conditions specifying the three-dimensional flow field come from ocean circulation models. Currently, the coupling between the nearfield plume and ocean circulation models is only in one direction (i.e., the nearfield model depends on the farfield flow field but not the reverse). This one-way coupling is also true between the farfield tracking and ocean circulation models. Because the nearfield plume induces a significant vertical velocity and the intrusion layer can generate a large flow rate (about 1,000 m^3/s for the primary intrusion during DWH), two-way coupling may be important between the buoyancy-dominated nearfield and intermediate-field (region of the intrusion formation) and the ocean circulation. For the DWH oil spill, the primary intrusion was at approximately 350 m above the source, but the elevation of the intrusion layer is determined by oceanographic conditions and other factors and may vary. (Socolofsky et al., 2011) Research groups are actively studying this problem, but to date, no two-way coupled hindcast simulations for the nearfield and the farfield of the DWH spill have been reported.

For a Lagrangian stochastic models, oil is typically represented by numerical particles, or Lagrangian elements, that are advected by mean ocean currents and droplet rise velocity, diffused by ambient turbulence, and transformed by a host of physical, chemical, and biological processes, including dissolution, biodegradation, sediment particle interactions, etc. While oil transformations are important for determining oil fate, we focus here on transport and mixing.

Typically, ocean circulation models, such as the SABGOM (South Atlantic Bight—Gulf of Mexico) model and HYCOM (Hybrid Coordinate Ocean Model), are used to provide detailed velocity fields. Transport models, such as LTRANS (Lagrangian Transport; North et al., 2015, used with SABGOM) and CMS (Connectivity Modeling System; Paris et al. [2012] used with HYCOM), then calculate oil transport based on local currents interpolated from the gridded circulation model velocities. Alternatively, circulation and transport can be calculated in an integrated model such as GNOME (General NOAA Operational Modeling Environment; Macfadyen et al. [2011]). Circulation models generate three-dimensional flow fields over complex bathymetry—often using nested domains that provide added resolution in critical areas—and may respond to tides, wind, air/sea fluxes, density variations, and Earth's rotation (Coriolis force), among others. Many ocean circulation models also rely on data assimilation (i.e., periodic updating of predictions using measurements, such as water levels from satellites) to keep model predictions on track.

The rise velocity of droplets is added to the advection from the ocean currents. Because smaller droplets rise more slowly than larger droplets, horizontal ocean currents stretch the spatial distribution of droplets in the horizontal dimension as they rise through the water column. The smallest droplets surface farthest from the source. Mitigation measures to reduce droplet size (e.g., subsea dispersant injection) or more energetic breakup regimes can cause the surface expression of the oil to move downstream relative to the unmitigated case (Socolofsky et al., 2015).

The total rise time of droplets and bubbles is the sum of the time spent in the buoyant plume plus the time it takes the individual droplet to rise the remaining distance to the surface. In deep water, the buoyant plume will be a few hundred meters above the source and take only about 30 minutes to transit regardless of droplet and bubble size. In contrast it can take several hours to many days for individual oil droplets to rise the remaining distance, depending on their size and density. Thus, accurately estimating the vertical velocity of individual droplets and bubbles is an important factor in modeling blowout and pipeline leaks in deep water.

A commonly used algorithm for calculating the rise velocity is based on the generalized Stokes' Law to include situations where the flow around the droplet is turbulent. The first application of this approach in the oil spill literature was done by Zhao et al. (2014a). The rise velocity also depends on the shape of the droplets and bubbles, and the algorithm is more elaborate (Zhao et al., 2016a; Zheng and Yapa, 2000).

There are several factors that can further affect the rise velocity that are still not routinely accounted for by most integrated spill models. The most well-established of these arises from the formation of a hydrate skin on the surface of a gas bubble formed in deep water as documented by Chen et al. (2014) and Rehder et al. (2009). This hydrate skin serves to stiffen the droplet surface and alter the drag calculated by the modified Stokes' Law. Gros et al. (2017) account for this effect in a farfield transport model. The second factor that may affect rise velocity is the presence of saturated gas in oil droplets released in deep water as described by Pesch et al. (2017). As mentioned earlier in this chapter, "live-oil" contains liquid oil saturated with gas (primarily methane). As live oil droplets rise through the water column, the pressure decreases and the temperature increases. As a result, the gas comes out of solution and may form bubbles that cling to the rising oil droplets. Pesch et al. (2017) label this as "internal de-gassing" and performed laboratory experiments and independent calculations that support their hypothesis. However, in order for this to occur in a DWH-like scenario, the rate of droplet ascent (implied by the rate of depressurization) would have to be quite high such that the gas formed bubbles before they could diffuse; evidence from the DWH suggests that most of the gas entered the intrusion as dissolved phase rather than ascending to the surface as bubbles. While measurements to date suggest little impact above the intrusion layer, the impact below the intrusion layer remains uncertain.

Farfield tracking models generally treat horizontal and vertical turbulent mixing using random walk (or similar) algorithms, as in Macfadyen et al. (2011), North et al. (2015), and Paris et al. (2012). One way to obtain diffusivities used in these models is from the horizontal and vertical turbulent diffusivities computed in the ocean circulation models. However, this presumes that diffusion is a Fickian process and the computed diffusivities may be artificially high in order to keep the circulation model stable. Another approach is to estimate diffusivities directly from field measurements of an introduced tracer. For example, Ledwell et al. (2016) measured concentrations of SF_5CF_3 introduced near the DWH site. In analyzing data from such experiments, horizontal ocean currents are usually assumed to be spatially uniform, in which case the unresolved spatial variability is manifest as a scale-dependent diffusivity (i.e., one that depends on the size of the tracer). Strongly variable currents can spread the tracer widely, and while the horizontal spreading of the tracer can be represented by a large diffusivity, details of the concentration distribution will be lost. A different approach was used by Wang et al. (2016c), who studied vertical mixing near the DWH site using a microstructure profiler to determine small-scale turbulent properties. Vertical mixing, in particular, has been found to be spatially variable (e.g., diffusivities in the thermocline are several orders of magnitude smaller than those near the surface or in the deeper abyssal waters).

In addition to contributing to droplet diffusion, turbulence can also alter droplet rise velocity dependent on the mass of the oil droplets (Maxey and Riley, 1983): very small droplets usually move with the flow and large droplets tend to withstand turbulent fluctuations impacting them. A range of droplet sizes could be impacted by turbulence through two mechanisms, which both depend on the density and the size of droplets with respect to turbulence intensity. The first mechanism is trajectory biasing, in which droplets tend to avoid intense vortices and thus could migrate through them causing the droplets to rise faster than their rise rate under quiescent conditions. This was observed by Friedman and Katz (2002). The second is vortex trapping, where a droplet in an eddy will tend to be displaced to its center due to inertia, because the droplet is lighter than the water in the eddy. This is the converse of a centrifuge, which pushes particles heavier than water to the outer edge. Comparing field measurements of turbulent velocities with droplet rise velocities, Wang et al. (2016c) concluded that droplets larger than 0.4 mm (rise velocity 6 mm/s) were unlikely to be significantly affected by turbulence, while those smaller than 0.04 mm (rise velocity 0.1 mm/s) were expected to become so entangled with turbulence that they might be permanently trapped below the surface.

FINDINGS AND RECOMMENDATIONS

Finding: Models and experiments using oil jets discharged to seawater consistently demonstrate that when dispersant is applied to oil releases deep beneath the water surface it can dramatically reduce (5-10 times) the droplet size. The interplays of subsea dispersant injection (SSDI) and other processes—such as the role of natural gas, and the flow field and pressure drop upstream of the release point—may be important, but are not completely understood or represented in existing models.

Finding: Droplet size is a major factor determining the fate and transport of oil spilled at depth. Both natural processes and the application of subsurface dispersants affect droplet size distributions (DSDs), in varying degrees. Small droplets take longer to rise to the surface and microdroplets may remain suspended in the water column. When oil droplets take longer to rise to the surface, processes such as dissolution and biodegradation have more time to alter the chemical composition of the oil that surfaces, reducing the transfer of volatile organic compounds (VOCs) to the atmosphere.

Finding: Existing droplet models have been compared to varying degrees with laboratory studies and the DeepSpill field experiment. The models have also been used to predict droplet sizes at *Deepwater Horizon* scales where they generally show a variation of about two times. Further modeling uncertainty derives from our lack of understanding of such processes as tip streaming, pressure gradients, and out-gassing.

Recommendation: Additional observations of droplet formation are needed as close to field scale as possible. An extensive, dedicated field study would be highly desirable; but, should cost and permitting prove prohibitive, a spill of opportunity should be considered. Field experiments will be inherently restricted in the phenomena that can be studied because of logistical challenges and open boundaries. They will also face legal and regulatory challenges. Thus, it would be highly desirable to develop a large-scale laboratory facility with the ability to include high ambient pressure and observation of droplets as they evolve over time.

Recommendation: Droplet models should be extended to further include large pressure gradients, the role of gas, and tip streaming.

Recommendation: In the event of another subsea release, droplet size near the source should be measured, as the technology is available.

Finding: Photochemical oxidation of oil may occur quickly (hours to days), potentially reducing the time window during which surface dispersant use is most effective.

Recommendation: Photochemical oxidation of oil will vary at different locations and at different times of the year. Therefore, the importance of this process needs to be examined for individual oil spill scenarios, oil types, and slick characteristics so that it may be considered for incorporation into oil spill response strategies.

Finding: The use of surface dispersants may enhance the formation of oil-containing marine snow leading to enhanced transport of oil to the deep sea.

Recommendation: End-to-end oil spill trajectory and fate models should simulate the sedimentation of oil spill residues with the inclusion of validated oil-containing marine snow formation mechanisms.

Finding: Oil transport on the water surface is different from that of neutrally buoyant material, as oil can gather in convergence zones and/or move relative to the water surface.

Recommendation: Oil spill models should account for sharp vertical and horizontal variations in oil transport.

Finding: The use of SSDI in a blowout hinges in part on whether it would reduce VOCs and enhance the safety of local response personnel. Depending on the exact scenario, SSDI can be effective at reducing VOC concentrations above the wellhead, although the specific details of atmospheric VOC dynamics remain uncertain.

Recommendation: A model hindcast of the VOCs generated around the Macondo well should be performed in order to better validate available models and to better understand the various processes affecting VOC concentrations.

Finding: Biodegradation is a key factor potentially impacted by dispersant application, both directly and indirectly.

Recommendation: Studies are needed to quantify the early stages of bacterial community response and development that precede rapid biodegradation as well as to further test the hypothesis that small droplets facilitate biodegradation through increasing the surface-area-to-volume ratio. The interactions of bacteria, photooxidation, emulsions, and dispersant efficacy should also be explored to understand the overall influence of dispersant use on biodegradation of oil.

Finding: The occurrence of natural gas in an oil well blowout can strongly impact discharge velocity and DSD and, therefore, environmental partitioning of discharge and associated weathering processes.

Recommendation: Additional modeling and experimental studies are needed at large scales and at high pressures to better define natural gas's impacts on subsea discharge and fate and transport processes.

Finding: The dissolution of surfactants from oil droplets occurs during buoyant rise associated with SSDI. However, different components of the dispersant formulation may dissolve at different rates, leading to molecular fractionation.

Recommendation: Industry or regulatory agencies should sponsor a study to determine how dissolution and molecular fractionation of dispersant may affect the behavior of oil at the surface following SSDI, particularly with respect to any impacts to the effectiveness of other response options.

CHAPTER 3

AQUATIC TOXICOLOGY AND BIOLOGICAL EFFECTS

INTRODUCTION

Difficult and time-sensitive decisions are made during an oil spill response to mitigate the environmental impacts of the spill. Under the appropriate conditions, these decisions may involve the use of dispersants, with a recognition that there are trade-offs associated with this and other response actions (see Chapters 5 and 6). Appropriate response decisions and trade-off evaluations require the inclusion of sound scientific information. In particular, assessing the ecological and toxicological consequences of dispersant use relies in part on findings from laboratory studies. Since the publication in 2005 of the National Research Council (NRC) study *Oil Spill Dispersants: Efficacy and Effects* (NRC, 2005), more than 100 research papers and reviews have been published that specifically address topics of the toxicity of oil, dispersants, and dispersed oil mixtures to various biota. Much of the increase in research activity was driven by the requirements of the Natural Resource Damage Assessment (NRDA) and related research in the wake of the *Deepwater Horizon* (DWH) oil spill (*Deepwater Horizon* Natural Resource Damage Assessment Trustees, 2016; Jones, 2010). The large volumes of dispersants used during this spill, particularly at depth (~1,500 m), has given rise to a number of renewed questions regarding the toxicity of untreated oil, dispersants, and, dispersed oil mixtures (*Deepwater Horizon* Natural Resource Damage Assessment Trustees, 2016; Kujawinski et al., 2011). One of the key questions to be resolved is the potential for enhanced bioavailability and toxicity of oil when dispersants are used, balanced against a reduction of potential exposure to surface oil. The proper design of tests that address this question directly, and the use of a correct dose metric for mixtures of oil components that exert toxicity, are central to a scientifically valid assessment.

Comparisons of the conditions of various large-scale spills also may lead to varying conclusions regarding bioavailability and potential toxicity, especially as they relate to the use of dispersants. For example, the chronic release from the former Taylor Energy site at lease block MC-20 and the DWH oil spill represent extremes of acute versus long-term chronic releases of oil into the environment. DWH was a deep release, extending for 87 days and covering a maximum surface extent of about 28,200 km^2 (MacDonald et al., 2015). The volume release rate was > 50,000 barrels (bbl) per day, resulting in contamination of an extensive oil volume extending from the surface to 1,500 m. By contrast, the MC-20 release is ongoing since 2004 (Warren et al., 2014; 15 years at the writing of this document). According to a recent satellite remote sensing survey (Sun et al., 2018), the MC-20 release routinely generates a surface slick extending about 15 km^2 (maximum spread of 1,900 km^2) from the MC-20 location, with an estimated volume discharge of 48 to 1,700 bbl per day. Both scenarios would seem suited for long-term study of exposure toxicity, especially for sessile and demersal animals; but, while the toxic effects of DWH have been extensively reviewed, there are no such published results for Taylor.

The case of the DWH oil spill illustrated the complex nature of a prolonged spill event as well as the potential for multiple pathways of exposure of biological resources to toxic oil compounds. These key considerations for assessing the toxicity of oil spills in relation to oil and dispersed oil are illustrated in Figure 3.1. Aquatic organisms were potentially exposed to physically- and chemically-dispersed oil due to the formation of deepwater plumes, to surface dispersed oil, and from rising and surfaced oil. Wind- and current-driven oil at the surface resulted in exposure of biological resources in offshore and coastal surface waters and, eventually, in estuaries and coastal barrier beaches. A secondary exposure of benthic ecosystems may have resulted from the formation of oiled marine snow (see Chapter 2), which eventually sank in the region around the wellhead, carrying with it dispersant residues and weathered oil components (Daly et al., 2016; Passow et al., 2012; Valentine et al., 2014). Volatile compounds from oil resulted in the elevated concentration of volatile organic compounds near the wellhead where air-breathing species (marine mammals and turtles) and response workers were potentially exposed. Adverse effects from oil can result from exposures to dissolved aqueous oil components, physical smothering from direct contact, and oil ingestion, inhalation, aspiration, and consumption of oiled prey (see Box 3.1), but these impacts vary by species, life stages, and behavior (e.g., seasonal migrations, benthic feeders).

This chapter synthesizes the state of knowledge on the toxicological effects of physically and chemically dispersed oil, particularly those published since the prior NRC report on dispersants (NRC, 2005), and with emphasis on studies emerging post-DWH. While the information synthesis presented in this chapter relies on recent knowledge, it is important to note that (1) continuous

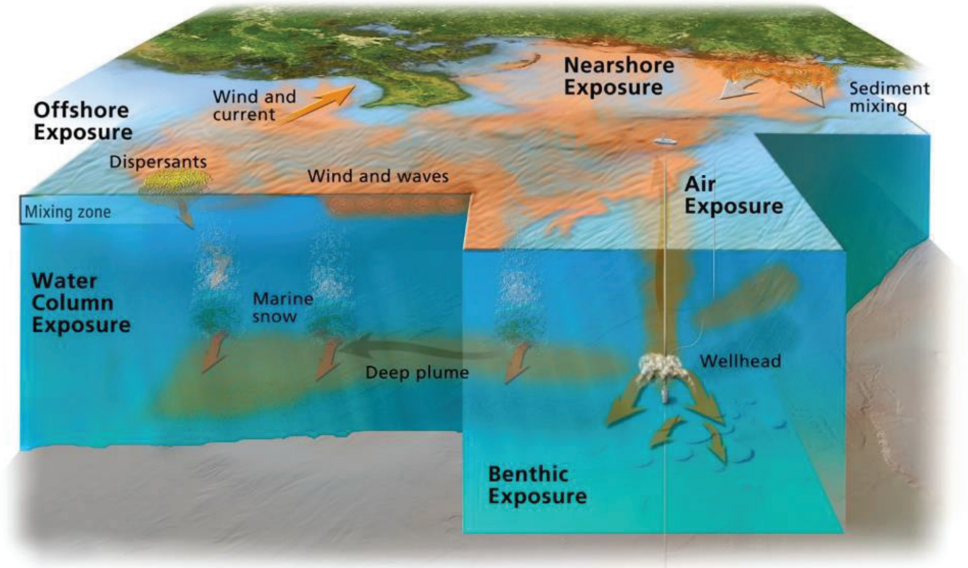

FIGURE 3.1 Potential routes of oil exposure resulting from a deepwater spill such as DWH. SOURCE: NOAA.

BOX 3.1
Routes of Exposure to Oil

Exposure of aquatic receptors to physically and/or chemically dispersed oil can occur through each of four basic routes, which may have different relative contributions to the overall exposure based on the biology of each biological resource.

Absorption from water—Aquatic organisms may be exposed to oil and oil residues in the water column via absorption of bioavailable hydrocarbon compounds directly through their outer membranes, skin, or respiratory membranes that are exposed to the dissolved concentrations.

Direct contact—Wildlife found at the air-water interface (e.g., sea turtles, mammals, birds) may come into direct dermal contact with oil when swimming, surfacing, or diving through surface oil, which would cause their bodies to become coated with oil. Oil on feathers or fur can damage waterproofing and insulating characteristics leading to hypothermia and possibly death. Depending on the amount, dermal contact with liquid oil can cause effects ranging from relatively innocuous to more severe impacts on sensitive tissues, particularly the eyes.

Inhalation and aspiration—While inhaling, air-breathing wildlife (e.g., sea turtles, mammals, birds), particularly those breathing above the air–water interface, may be exposed to volatile organic compounds and potentially to oil droplets aerosolized above surface slicks by breaking waves, wind, and rain. Cetaceans may also incidentally aspire seawater containing liquid oil into their lungs. Both inhalation and aspiration of oil may cause irritation of the respiratory tract and could serve as a source of hydrocarbon compounds in the bloodstream.

Ingestion—Aquatic organisms may be exposed to oil or oil residues through the ingestion of water, sediments, and/or food containing oil or water containing microdroplets of oil. While some oil fractions are insoluble in the fluids of the gastrointestinal tract, other more soluble fractions are absorbed and transported into the bloodstream. Depending on the amount ingested, oil can cause irritation of the gastrointestinal tract.

deepwater releases such as the DWH oil spill are atypical and not representative of most spills; (2) when considering the toxicity associated with dispersant use, the baseline for comparison is untreated oil as opposed to a pristine environment; and (3) dispersants are not a viable response option for most spills in marine U.S. waters, as the vast majority of surface or deepwater oil spills are either too small or too close to shore for dispersant use because of the logistical complexity of a dispersant operation and potential harm to coastal resources and interactions with people (see Chapters 1 and 6).

This chapter first discusses the aquatic toxicity (absorption) and then the biological effects (direct contact, inhalation and aspiration, and ingestion) on exposed organisms. Because of the challenges in differentiating the biological effects of an oil spill with and without dispersant use under field conditions, the primary focus of this chapter is on aquatic toxicity as determined using laboratory tests. Finally, it provides context of toxicity in relation to observed field exposures and discusses potential future advances in the field of oil and dispersed oil toxicity testing. This chapter also identifies areas of uncertainty and outstanding questions, and it makes recommendations for additional studies that could fill critical gaps.

Despite the existence of recommended toxicity testing protocols developed by the Chemical Response to Oil Spills Ecological Effects Research Forum program (CROSERF; Aurand and Coelho, 2005), a review of the existing toxicity studies identified a wide variety in the methods used, including differences in media preparations, exposure methods, and chemical analyses. As a result, there is no straightforward, consistent means of assessing the central question: whether exposure media containing chemically dispersed oil is more or less toxic than exposure media containing physically dispersed oil.

The committee evaluated two approaches to addressing this question. The first approach is based on the results of toxicity tests using the variable loading toxicity test design. As shown below, this test design can directly assess the difference in toxicity due to the presence of dispersants. The second approach is based on a combination of experimental data with a controlled design and modeling analysis. In particular, models have been developed that can predict the toxicity of oil of varying compositions to a wide variety of organisms (e.g., PETROTOX and Oiltox; as discussed below). This new capability permits a reassessment of the conclusions drawn from the previously available and newly published toxicity data. Finally, recommendations regarding research gaps, priorities for additional research, and "good practices" for the conduct of controlled exposure trials and in situ monitoring are provided.

The methods the committee recommends at the end of this chapter represent a paradigm shift away from developing toxicity tests that attempt to reproduce field exposure conditions. Instead, the committee recommends focusing effort on methods that consistently produce toxicity test results required for calibration and validation of toxicity models at environmentally realistic levels based on concentrations measured in samples from the field during a spill. The toxicity models are then used together with environmental fate models discussed in Chapters 2, 6, and 7 to evaluate the exposure and toxicity associated with various response options, in particular, the potential costs and benefits of dispersant use.

AQUATIC TOXICOLOGY

Research on the toxicity of oil and dispersed oil mixtures has used a wide variety of test biota (mostly invertebrates and fish) exposed to varying dispersant-to-oil ratios (DORs), under varying environmental conditions (e.g., laboratory, mesocosm, field) and varying physical conditions (e.g., temperature, salinity, etc.). Most of the previous studies have been single-exposure design, varying in exposure time and concentrations, measuring lethal and sublethal effects over experimental periods ranging from hours to weeks. Most often, the observation period has been on the order of several days, with the most common being 24-, 48-, and 96-hour experiments. The extrapolation of data from laboratory- or mesocosm-based studies requires calibrating the exposure duration and concentrations from these highly controlled studies to the mosaic of exposure conditions experienced in actual oil spills. This includes different exposure vectors (e.g., exposure to contaminated water, food, and sediments). Thus, when interpreting environmental impacts from actual spills, the baselines (e.g., background concentrations), environmental concentrations, and biodegradation of toxic compounds all are critical elements in estimating real-world toxicity.

A meta-analysis of laboratory studies on the toxicity of dispersants and of studies evaluating the toxicity of both physically and chemically dispersed oil was undertaken following the selection criteria summarized in Appendix F. This meta-analysis focused on studies published between 2005 and 2018, with studies published between 2005 and 2012 obtained from an existing data repository (Bejarano et al., 2016; NOAA ERD, 2015). While most of the data included in this meta-analysis build on the wealth of knowledge generated as a result of the DWH oil spill, data interpretations should not be taken as a reevaluation of damages as performed by the spill's Natural Resource Trustees. The primary goal of this evaluation is to address the central question of whether exposure media containing chemically dispersed oil is more or less toxic than is exposure media containing physically dispersed oil, and to demonstrate challenges in interpreting toxicity data which were previously limited (NRC, 1989, 2005) by the availability of quantitative information. Box 3.2 includes definitions of toxicological terms and acronyms used in this chapter.

BOX 3.2
Aquatic Toxicology Terms Used in This Chapter

Exposure Regimes:

Flow-Through Exposures—Tests where aquatic species are exposed to media pumped continuously into a dilutor system and then to the test vessels. This exposure regime is used to maintain relatively constant concentration throughout the test duration.

Spiked Exposures—Tests where aquatic species are exposed to concentrations that are highest at the start of the exposure period, with declining concentrations to nondetectable levels after 6-8 hours.

Static Exposures (with or without open vessels)—Toxicity tests where aquatic species are exposed to the same media for the test duration (static nonrenewal) or to fresh media partially or completely renewed at prescribed time intervals (static renewal). Exposure concentrations may change during the test due to biological uptake, volatilization, chemical degradation, etc.

Exposure Types:

Acute Toxicity—Acute toxicity to aquatic organisms estimated from relatively short exposures, generally ≤ 96 hours.

Chronic Toxicity—Chronic toxicity to aquatic organisms estimated from exposures that occur over an extended period of time or over a significant fraction of a lifetime (generally days to weeks).

Mixing Method: The method employed to prepare an aqueous solution for testing the partially miscible oil or dispersant-oil mixture.

Water-Accommodated Fraction (WAF)—The solution that is decanted from under the floating bulk oil after mixing is complete and the oil is allowed to separate. The WAF is composed of the *aqueous phase*, which does not contain microdroplets, and the *oil phase*, which exists as microdroplets.

CEWAF—**C**hemically **E**nhanced WAF prepared by gently mixing oil and chemical dispersants in water.

LEWAF, MEWAF, HEWAF—WAFs prepared using **L**ow, **M**edium, or **H**igh physical energy mixing, respectively, of oil and water. Generally, LEWAF is generated with zero to < 10% vortex; MEWAF is generated using a 10%-25% vortex; and HEWAF is generated with > 25% vortex, or prepared in a blender at low speed.

Oil Dosing Method: The method employed to prepare the series of exposure treatments used to investigate dose-response and determine toxicity test endpoints.

Passive Dosing—Toxicity tests of WAF or CEWAF derived from a separation technique that relies on a permeable media (e.g., sand, polymer) to deliver the bioavailable (dissolved) hydrocarbons from the oil phase into the aqueous exposure media without the oil droplets that result from physical mixing methods.

Variable Dilution—Toxicity tests of WAF or CEWAF performed with oil doses derived from a dilution series of a stock WAF prepared at a single high oil loading.

Variable Loading—Toxicity tests performed using individually prepared WAFs or CEWAFs with an increasing amount of oil added to the aqueous phase. The resulting concentration is expressed as oil loadings (mg/L water).

Oil Phases:

Dissolved Concentration—The mass of dissolved component per unit volume, as discussed in Chapter 2. "Dissolved" is used to distinguish from "total" mass of a component that would equal the dissolved + immiscible droplets + components sorbed to particles. It is also referred to as "truly" dissolved concentration.

Microdroplets[a]—For the purposes of this chapter, microdroplets are droplets of oil that are immiscible in water. They can vary in size from nanometer to millimeter diameters.

continued

BOX 3.2 Continued

Species Evaluation Endpoints:

Acute HC5—The HC5 uses the toxicant's **Acute** LC50 as the effect concentration for constructing the SSD. Therefore, 5% of the tested species have their LC50 at this or lower concentrations, and 95% of the species have an LC50 greater than the Acute HC5.

Chronic HC5—The chronic HC5 uses species toxicity tests of longer duration than the acute exposure, approaching a lifetime or several reproduction cycles. The endpoints are sublethal, that consider growth and reproduction, and in some cases other important endpoints.

HC5—The fifth percentile toxicant concentration derived from an SSD. The **H**azard **C**oncentration **5**% is the toxicant concentration at which the most sensitive 5% of the tested species experience the toxic endpoint. The other 95% are not affected.

SSD—**S**pecies **S**ensitivity **D**istribution. The probability distribution of a toxic effect concentration (e.g., LC50s) for a specific toxicant across multiple species. The SSD is used to quantify the variation in species sensitivity to a particular toxicant at a specific exposure duration.

Toxicity Endpoints:

ECp—Effect concentration that causes sublethal or lethal effects in a given percent (p) of the exposed test population. The typical reported endpoint, primarily from chronic toxicity tests, is the EC50, or the median effects concentration that causes an effect to 50% of the exposed organisms at a specific exposure duration (i.e., 96-hour EC50). Responses may include changes in growth, development, reproduction, biochemistry, physiology, and behavior.

LCp—Lethal concentration that causes death to a given percent (p) of the exposed test population. The most typically reported endpoint, primarily from acute toxicity tests, is the LC50, or the median lethal concentration that causes death to 50% of the exposed organisms at a specific exposure duration (i.e., 96-hour LC50).

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[a] The committee recognizes that microdroplets may be defined differently for other purposes. Elsewhere in this report, the committee loosely refers to microdroplets as droplets smaller than approximately 70 microns (μm). (See Chapter 2 for more information on droplet sizes.) The definition provided here is for the purpose of this chapter.

SOURCES: Aurand and Coelho, 2005; *Deepwater Horizon* Natural Resource Assessment Trustees, 2016; Rand and Petrocelli, 1985.

Toxicity of Dispersants in Aquatic Exposures

For as long as dispersants have been used, the toxicity of dispersants and dispersed oil has been the topic of controversy (NRC, 1989, 2005). Dispersant formulations have evolved over the last decades, and the current generation of commercially available dispersants (e.g., Dasic Slickgone, Finasol® OSR52, and Corexit® 9500) contain less harmful chemical constituents than older dispersants (NRC, 1989, 2005). Modern formulations contain nonaromatic hydrocarbons or water-miscible solvents (e.g., ethylene glycol or glycol ethers) and nonionic and/or anionic surfactants. Changes in dispersant formulations aimed at reducing toxicity warrant a brief overview of dispersant-only toxicity data. Such data are used for regulatory approvals to allow dispersant use and for evaluating the toxicity of oil-dispersant mixtures because the toxicity of dispersant alone must be considered.

With the exception of some of the data collected by CROSERF, most dispersant-only toxicity data generated since 2005 used constant static or static renewal tests. A total of 318 unique toxicity records from constant exposure experiments for 68 aquatic species (mostly marine species) were generated between 2015 and 2017 for nine dispersant formulations, with data for Corexit® 9500 accounting for nearly half of all toxicity data (reviewed in Bejarano, 2018). Early life stages, which are generally considered to be the most sensitive, accounted for 43% of all records followed by juveniles and adults (30% and 26%, respectively).

Figure 3.2 is a plot of the acute HC5 concentrations for nine dispersants (Bejarano, 2018; see Box 3.2 for definitions). The acute HC5s range from approximately 1 to 15 mg/L (ppm). While

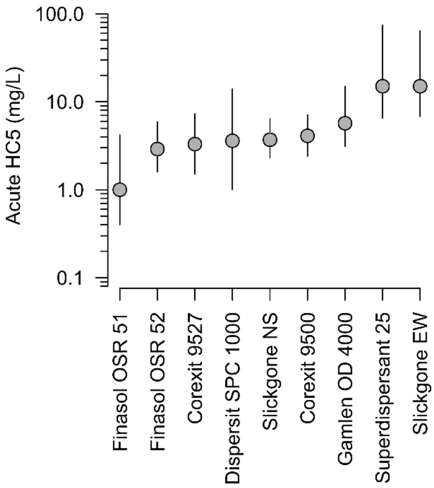

FIGURE 3.2 Acute HC5 and confidence limits for nine dispersants. SOURCE: Data from Table 2 in Bejarano, 2018.

a much larger species diversity has been used in more recent toxicity testing (e.g., Echols et al., 2018), the documented HC5 has remained comparable to previously reported data (Barron et al., 2013; Bejarano, 2018; Bejarano et al., 2016). These HC5s are generally protective for the survival of the most sensitive species (Hemmer et al., 2010; Judson et al., 2010). While most dispersant-only toxicity data are for marine species, freshwater species appear to fall within the same range of sensitivity; thus, HC5 may also be protective for species in freshwater environments (Bejarano, 2018).

These HC5s are derived from dispersant-specific species sensitivity distributions (SSDs) that can be examined for the relative sensitivity of each aquatic species. For example, it is often assumed that shallow-water corals are one of the most sensitive taxonomic groups, but based on limited information for three species, their sensitivities fall within the middle to upper portions of the SSDs and are not grouped toward lower percentiles (Bejarano, 2018).

The data discussed above reflect constant concentration exposures. In some cases, declining concentration (i.e., spiked flow-through) tests with a half-life of ~2.5 hours have been conducted to mimic some field conditions (e.g., Aurand and Coelho, 2005; Clark et al., 2001). Analysis of these studies yielded an HC5 for Corexit® 9500 of 65.8 mg/L (95% confidence interval [CI]: 29.1-299 mg/L), which is 16 times higher than the acute HC5 resulting from 96-hour exposure: 4.1 mg/L (95% CI 2.4-7.1 mg/L). Furthermore, based on operational dispersant application rates (at least at the surface), dispersant-only concentrations are expected to range for minutes to several hours and between 3 and 10 mg/L depending on the characteristics of the application (NRC, 1989). These results, together with previous assessments (NRC, 1989, 2005), clearly point to the need to focus on the hazard posed by physically and chemically dispersed oil, not on the dispersants themselves. The key issue for dispersant use, as was underscored in the previous NRC dispersant studies (NRC, 1989, 2005), is whether the toxicity and exposure potential of untreated oil are less than or greater than that of dispersed oil under actual field conditions and in laboratory toxicity investigations.

Measuring the Toxicity of Oil

Determining the toxicity of oil from aquatic exposures for both physically and chemically dispersed oil is complicated not only by the idiosyncrasies of test conditions used in most studies

(Aurand and Coelho, 2005; Bejarano et al., 2014b; Coelho et al., 2013; NRC, 2005; Redman and Parkerton, 2015) but also by the complex composition and properties of oil. In particular, the following facts need to be considered:

1. Separation of the aqueous phase from the bulk oil phase is difficult because oil is an immiscible liquid. Without a physical separation device such as a dialysis membrane, only the density differences can be employed to achieve the phase separation.
2. Oil is a mixture of thousands of compounds of widely varying physical and chemical properties, and this complexity both within a single oil and especially across different types of oils influences the toxicity that results.
3. Oil is only partially soluble in water. The different compounds dissolve in amounts that vary over five orders of magnitude. The actual amounts are determined by the component concentrations in the oil.
4. Determining the dissolved component concentrations in the aqueous phase is difficult because of residual small oil microdroplets that remain in the aqueous phase due to incomplete separation of the aqueous phase from the bulk oil phase.

Because the appropriate interpretation of toxicity data hinges on the testing method used and the degree to which these factors have been appropriately addressed, testing protocols will be discussed first. Toxicity testing protocols consist of three main elements: media preparation, exposure, and chemical characterization. One of the more difficult to resolve aspects is media preparation, which is described in detail below.

Media Preparation

Preparation of WAFs

To evaluate the toxicity of a given oil it is necessary to prepare a test media for the organism exposure. The test medium is composed of a mixture of oil and seawater (simply referred to as "water" in the following discussion) at a specific concentration of oil (e.g., 100 mg oil/L). Mixing is provided for a long enough period of time to attain a reproducible suspension. When oil mixes with water, there is a quantity of liquid oil that remains in the aqueous phase after separation. This is unavoidable because the oil and water have similar densities and some energy must be introduced into the mixture to promote equilibration. Depending on the magnitude of mixing energy, the undissolved remaining oil is distributed in a range of oil droplet sizes, from millimeter to micrometer diameters. These remaining oil droplets are referred to collectively as microdroplets.[1] After separation, the resulting aqueous phase is referred to as a water-accommodated fraction, or WAF (see Box 3.2). The WAF is a two-phase system: the oil phase, comprised of microdroplets, and the aqueous phase, comprised of water and the dissolved oil components.

Because the test media is comprised of two phases (oil and aqueous), both the mixing energy used (e.g., low, medium, or high) and the method for preparing the concentration series for the WAFs to be tested have the potential to influence the presence, concentration, and size of microdroplets. These definitions are used in the following section:

Dissolved Concentrations—the concentration of oil components in only the aqueous phase. This has also been referred to as "truly" or "freely" dissolved components.

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[1] As explained in Box 3.2 and the corresponding footnote, this definition is for the purposes of this chapter.

Total Concentrations—the sum of the concentration of oil components in the aqueous phase and the oil phase. It is the mass of oil contained in the aqueous phase and in the microdroplets per unit bulk volume of solution.

Method for Creating a Concentration Series: The Effects of Microdroplets

Two different methods have commonly been used to create exposure treatments for toxicity tests: variable loading and variable dilution (NRC, 2005). While the pros and cons of each of these methods have been extensively discussed (Aurand and Coelho, 2005; Barron and Ka'aihue, 2003; NRC, 2005; Redman and Parkerton, 2015; Singer et al., 2000, 2001), there does not appear to be a consensus among the scientific community on a preferred approach. In order to decide which design is preferable, a discussion is presented below that evaluates concentrations that result from variable loading and variable dilution experimental procedures.

Variable Loading

Variable loading toxicity tests consist of a series of individually prepared solutions at variable concentrations of oil (mg oil/L water) used to create a series of loadings, for example, 100, 50, 25, …, 0.25 mg oil/L. The loading level that results in a 50% mortality to the test organisms is known as the lethal loading 50 (LL50). It is found by fitting a dose response curve to the observed mortality versus loading. The discussion below focuses on the effect that the presence of microdroplets has on the resulting toxicity.

Consider a comparison of a physically dispersed LEWAF (see top row of Figure 3.3) and a chemically dispersed CEWAF oil (see bottom row of Figure 3.3). The initial state of the bulk oil-water system is shown in Figure 3.3A and B: oil floating on water. After physical (C) and chemical (D) dispersion, oil droplets are formed. Note that the chemically dispersed oil has a higher concentration of microdroplets. The aqueous phase is separated, resulting in the physically (E) and chemically (F) dispersed WAFs (LEWAF and CEWAF, respectively).

The mass of oil is the same in each vessel (C and D) before the solution is decanted from the bulk floating oil. Once the solutions are mixed for a sufficient time to achieve equilibrium, the dissolved concentrations of each component are the same in (C) and (D). The reason is that the *mass* of oil is equal in both vessels, and therefore the quantity of material that dissolves into the aqueous phase is the same. The critical point is that the state of disaggregation of the oil—that is, the concentration of microdroplets—does not affect the resulting *dissolved* concentration of oil components at equilibrium. It is controlled only by the mass of oil, which is the same in (C) and (D).

The WAFs are prepared by decanting the mixture of aqueous phase and microdroplets from the bulk oil to create the final LEWAF (E) and CEWAF (F) used for the exposure phase of the toxicity test. These two solutions, LEWAF (E) and CEWAF (F), have the same dissolved concentrations because a removal of a portion of the oil phase does not affect the equilibrium dissolved concentration. However, they have different total concentrations because the concentration of microdroplets is larger in the CEWAF. This difference has important consequences when the toxicities of these two solutions are compared in order to judge whether CEWAFs are more or less toxic than LEWAFs. The equality of dissolved concentrations is documented in a recent study by Forth et al. (2017) that compared total polycyclic aromatic hydrocarbon (PAH) dissolved concentrations from filtered samples of LEWAF, CEWAF, and HEWAF (see Figure 3.4). The remaining differences may be due to the degree to which filtering removes the microdroplets and the possibility that filtering alters the dissolved concentrations by sorption to the filter.

The difference in total concentrations between WAF and CEWAF can be used to test directly whether the differing concentrations of microdroplets change the toxicity of the WAFs. Figure 3.5 pres-

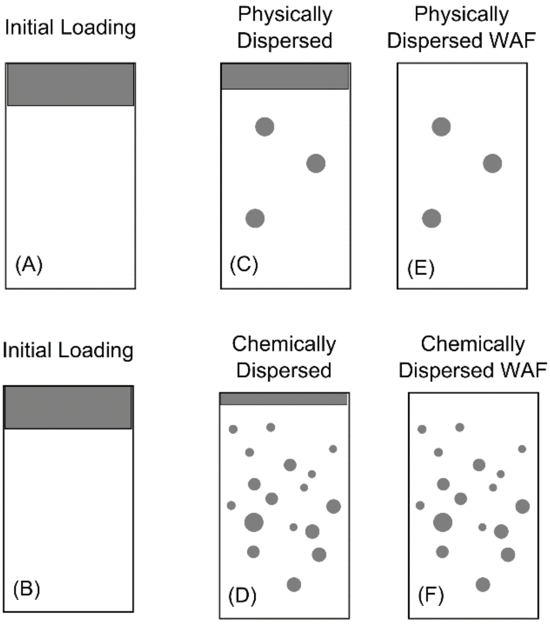

FIGURE 3.3 Diagrams of the state of two oil-water systems with different degrees of dispersion and the same oil loading. (A and B) the initial state before mixing; (C and D) after mixing has been completed; (E and F) after the WAF has been extracted. The top row depicts LEWAF and the bottom row depicts CEWAF.

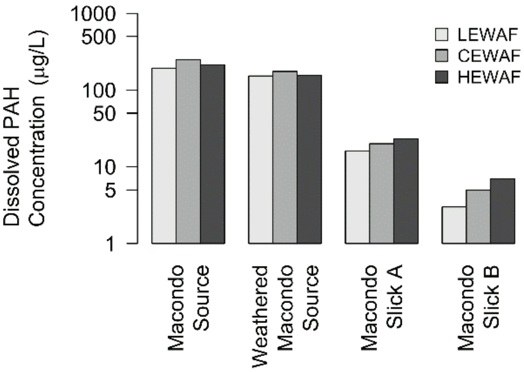

FIGURE 3.4 Comparisons of four oils: Macondo, Weathered Macondo, Macondo Slick A, and Macondo Slick B. Weathered Macondo is artificially weathered Macondo, whereas Macondo Slick A and Macondo Slick B are heavily weathered samples collected from the field. Three WAF types were generated: Low-energy mixing LEWAF, chemically enhanced CEWAF, and high-energy mixing HEWAF. The dissolved concentrations are measured from filtered samples. The concentrations are the arithmetic sum of the polycyclic aromatic hydrocarbons (PAHs). SOURCE: Data from Forth et al., 2017b.

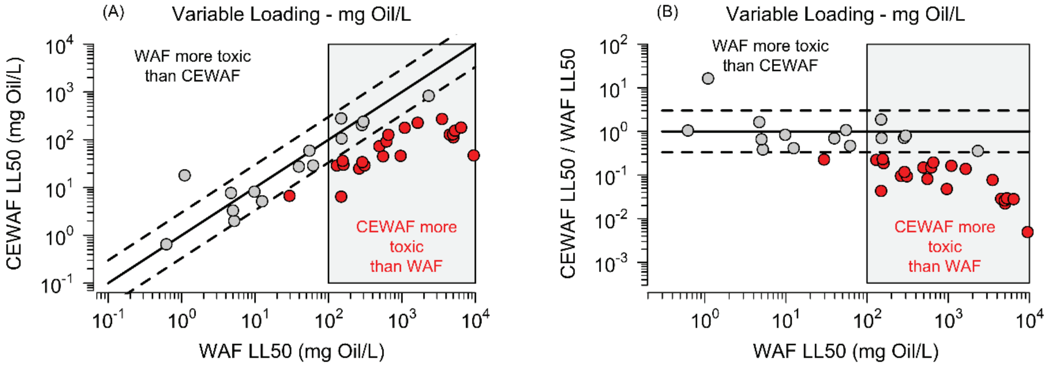

FIGURE 3.5 (A) Comparison of the median lethal (LL50) or effects-loading concentrations (EL50) for chemically dispersed CEWAF to physically dispersed WAF. (B) Ratio of CEWAF to WAF LL50 concentrations versus WAF LL50 concentrations. Only data from 1:10 and 1:20 dispersant-to-oil ratio are included. Dashed lines span a factor of 1/3 to 3 around the solid 1:1 line. Note the scale change on the vertical axis between figure (A) and figure (B). SOURCES: Data from Bejarano et al., 2014a, and the committee's meta-analysis (see Appendix F).

ents the available data from parallel variable loading experiments comparing CEWAFs (prepared with Corexit® 9500) to WAFs.

Figure 3.5A compares the LL50 lethal loading concentrations, the concentration of oil that causes 50% mortality for the CEWAF and WAF experiments. Figure 3.5B compares the ratio of CEWAF to WAF LL50s. In both cases, the solid line denotes equality of concentrations and the dashed lines are a factor of 1/3 and 3 variation. The red points denote experiments in which the CEWAF LL50 concentrations are less than the WAF LL50 by a factor of three, indicating that the presence of dispersant has increased the toxicity because a lower concentration causes 50% mortality. This analysis indicates that at lethal loadings less than approximately 100 mg oil/L, the addition of Corexit® 9500 does not affect toxicity. This is an important result because field measured concentrations during oil spills are typically well below this concentration. In contrast, for lethal loadings greater than approximately 100 mg oil/L, the CEWAF LL50 is lower than the WAF LL50 by at least a factor of 3. The difference is due either to the presence of more microdroplets in higher concentrations in the CEWAF relative to WAF, or that the concentration of Corexit® 9500 is high enough in the CEWAFs for it to be increasing toxicity. At 100 mg oil/L and the highest DOR used in these tests (1:20), the concentration of Corexit® 9500 would be 20 mg/L, which is above its acute HC5 (4.1 mg/L; see Figure 3.2). This suggests that at higher loading concentrations Corexit® 9500 could be contributing to the additional toxicity. However, a more detailed investigation is required in order to separate these effects more reliably.

The advantage of the variable loading method when creating test solutions is that it provides an initial answer to the central question posed in this chapter: whether exposure media containing chemically dispersed oil is more or less toxic than exposure media containing physically dispersed oil. Based on the committee's current analysis of this limited data, the answer is that at loadings below approximately 100 mg oil/L, when the solutions are at equilibrium, the toxicity of the WAF is equivalent to the CEWAF. Note that the CEWAF solutions will reach equilibrium faster than WAF solutions due to the larger surface area of smaller microdroplets. However, at equilibrium, the addition of dispersant does not appear to increase the toxicity of the oil at loadings below approximately 100 mg oil/L. It should be pointed out that this is a first attempt at answering this central question with the data that are available and that can be used to provide an answer that is not confounded by other complications.

Variable Dilution

The majority of toxicity tests conducted since the DWH spill have been performed using variable dilution. In this method, rather than preparing individual solutions via the variable loading method described in the previous section, a single stock solution is prepared at a high oil loading (e.g., 1,000 mg oil/L) and a WAF is prepared. This single WAF solution is progressively diluted to create a series of different concentrations as depicted in Figure 3.6. The concentration of oil is equilibrated (see Figure 3.6A), and a series of WAFs is made by serially diluting the aqueous phase plus microdroplets (see Figures 3.6B, C, and D).

The reason why this method is thought to be attractive is that it is assumed that only the WAF produced initially (see Figure 3.6B) needs to be chemically analyzed, reducing the costs for analytical chemistry. The concentrations of all the dissolved components in the WAFs for the subsequent dilutions (see Figures 3.6C and D) are estimated by multiplying the measured concentrations in the original WAF (see Figure 3.6B) by the dilution factor.

However, when microdroplets are present, they invalidate the assumption that the dissolved concentrations can be estimated using the dilution factor (as also discussed in Chapter 2). The dissolved concentrations in (A) and (B) are the same because steady-state has been achieved and separating the WAF from the bulk oil does not disturb the dissolved concentrations. The diluted WAFs (C and D) have a smaller microdroplet and dissolved concentrations because new uncontamined water is added to (C) and (D). As the system approaches a new equilibrium, the dissolved concentrations increase and the component concentrations in the microdroplets decrease. The reason why is that when the WAF is initially diluted the dissolved concentrations of the oil components decrease. This disrupts the equilibrium between the microdroplet oil and aqueous phases in (B), which causes an additional dissolution of oil components from the microdroplets to the aqueous phase, as also described in Chapter 2. This increases the dissolved concentrations and decreases the microdroplet concentration and composition until equilibrium is again achieved. As a consequence, the dissolved concentration does not decrease in proportion to the dilution.

As shown subsequently, the difference between the dissolved concentrations estimated by dilution and the actual dissolved concentrations can exceed one to two orders of magnitudes depending on the concentration of microdroplets in the WAF. As a result, comparing parallel variable dilution experiments with or without a dispersant cannot be used to distinguish unambiguously the effect of the dispersant. In summary, the microdroplets serve as a buffer for delivering and maintaining hydrocarbons in the aqueous phase. They are a source of dissolved constituents that reach an equilibrium after each dilution. Therefore, the dissolved concentrations at equilibrium are higher than that expected by the dilution process alone.

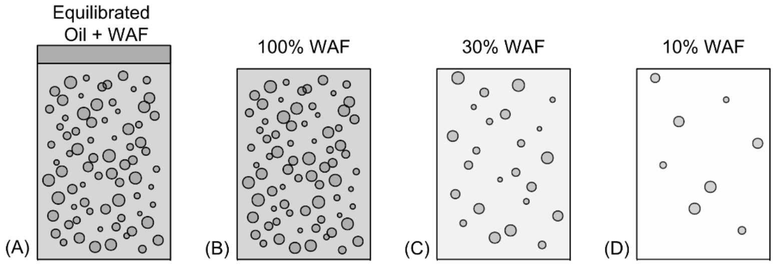

FIGURE 3.6 Schematic diagram of the preparation of the variable dilution exposure media. (A) The equilibrated initial solution. (B) The 100% WAF, which is the stock solution. (C) A 30% dilution. (D) A 10% dilution. (C) and (D) illustrate the situation when a fraction of the WAF has been added to the new test vessels. The dissolved (shaded) and microdroplet concentrations have been reduced by the dilution.

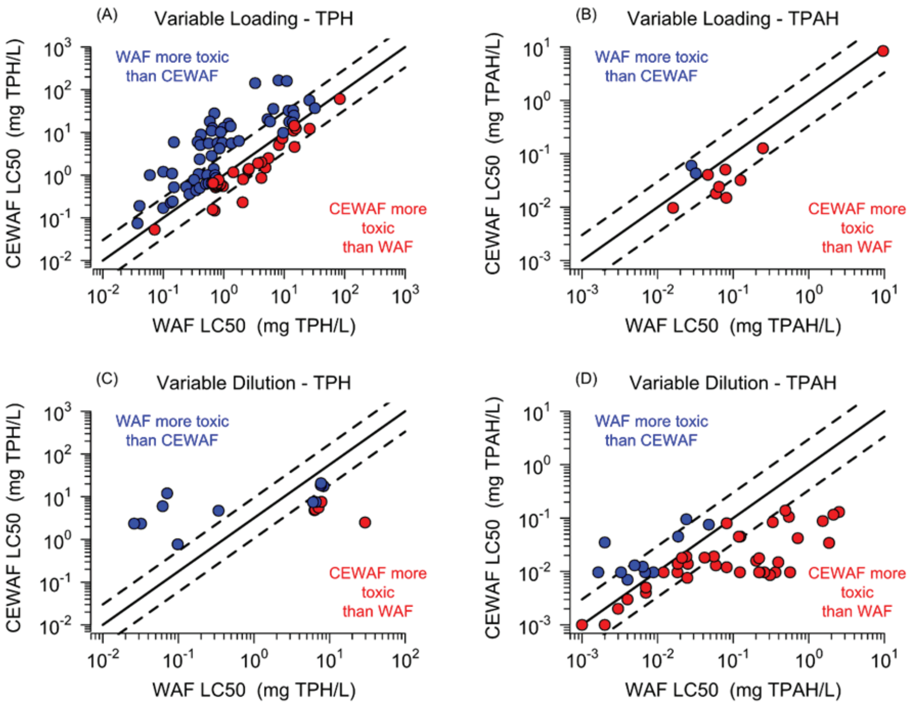

FIGURE 3.7 Paired toxicity data of CEWAF LC50 versus WAF LC50. Top row (A, B): data from variable loading experiments. Bottom row (C, D): data from variable dilution experiments. Left-hand column (A, C): concentrations are unfiltered total petroleum hydrocarbon concentrations. Right-hand column (B, D): concentrations are unfiltered total petroleum aromatic hydrocarbon concentrations. The solid line is 1:1 and dashed lines are a factor of 1/3 and 3 variation. Blue filled points CEWAF LC50 > WAF LC50 indicating that WAF is more toxic than CEWAF. Red filled points WAF LC50 > CEWAF LC50 indicating that CEWAF is more toxic than WAF. SOURCES: Data from Bejarano et al., 2014a, augmented with data from the committee's meta-analysis (see Appendix F).

The problem can be seen in the comparison made in Figure 3.7. This comparison is analogous to that presented in Figure 3.5, where parallel variable loading CEWAFs and LEWAFs test results are cross plotted. However, instead of expressing toxicity in terms of LL50s, lethal concentrations (LC50s) are adopted as the exposure metric.

Because there are many individual oil components in the aqueous phase, a "concentration" needs to be defined. Two different concentrations are used to quantify the amount of oil components present in the WAF or CEWAF. Total petroleum hydrocarbons (TPHs) is the arithmetic sum of the concentrations (mg component/L) of either all the hydrocarbon components measured or determined analytically as a group. Total polycyclic aromatic hydrocarbons (TPAHs) are restricted to the arithmetic sum of only the aromatic hydrocarbons, and in some cases to only PAHs with two or more rings. The implicit assumption is that each component is equally toxic and that the arithmetic sum is the proper parameter or dose metric that correctly predicts the toxicity of the mixture. This is not a valid assumption because the toxicity of the various components of oil vary by up to four orders of magnitude. Their toxicity is discussed in more detail subsequently in the section "Toxicity of Mixtures."

The top row of Figure 3.7 (A and B) compares the data from variable loading experiments where the LC50s are either TPH concentrations (A) or TPAH concentrations (B). The bottom row (C and D) compares the data from variable dilution experiments where the concentrations are either

(C) TPH or (D) TPAH. All the concentrations are from unfiltered samples. The solid line is 1:1 and the dashed lines are factors of 1/3 to 3 variation. Blue points denote CEWAF LC50 > WAF LC50 indicating that WAF is more toxic than CEWAF. Red points denote WAF LC50 > CEWAF LC50 indicating that CEWAF is more toxic than WAF.

For the variable loading experiments (top row), the TPH LC50s (A) scatter about the 1:1 line, with the WAF somewhat more toxic than the CEWAF. This appears to contradict the results from the variable loading experiments (see Figure 3.5) that used lethal loading LLC50s as the dose metric. However, depending on the analytical method used, the TPH measurement may include all the oil in the sample, including the residual bulk oil, and therefore be equal to the oil loading used in the test. Therefore, for the variable loading tests the TPH LC50 may approximate the LLC50s. One would expect that Figure 3.7A would give a similar result: no increased toxicity in CEWAFs relative to WAFs because all concentrations are < 100 mg oil/L. It is unclear why the data in Figure 3.7A indicate that the WAF is more toxic than the CEWAF.

Though based on a smaller number of test results, the comparison using TPAH LC50s (B) indicates the reverse. This suggests that TPH and TPAH concentrations are not directly related to the observed toxicity. They are arithmetic sums of concentrations that bear no relationship to the toxicity of the individual compounds in the sum and are unlikely to represent all the petroleum components that influence the toxicity. Because the components vary widely in toxicity, the arithmetic sum is not a precise aggregate representation of the cumulative toxicity present. This problem will be discussed later in this chapter, when the concept of toxic units (TUs) is introduced as the appropriate aggregate measure of the toxicity of the mixture.

The bottom row of Figure 3.7 compares the results for variable dilution experiments. The TPH comparison (C) suggests that WAFs are more toxic than CEWAFs, while the TPAH comparison (D) indicates the reverse. The data are widely scattered and contradictory. There are two problems with the variable dilution experiments. The first is in common with the variable loading experiment LC50s, namely, that TPH and TPAH are not sensible aggregates that adequately index toxicity. The second and apparently more serious problem is that the concentrations of each of the components are estimated from the dilution factor. As highlighted above, large errors result due to microdroplet dissolution. This point is discussed further later in the chapter. It is clear from these results that these toxicity data in their present form cannot be used to determine if exposure media containing chemically dispersed oil is more or less toxic than that containing physically dispersed oil. Variable dilution WAF and CEWAF tests can be objectively compared if the dissolved concentration and composition of the components are measured at each dilution step instead of being estimated from the dilution factor. For the variable loading experiments, the minimum chemistry required is the total oil and dispersant concentrations to ensure that the nominal quantities had in fact been added.

Some experiments have been performed where the samples were measured for total concentrations and then filtered to measure dissolved concentrations. The results are presented in Figure 3.8. The aggregate is TPAH50, the arithmetic sum of 50 PAHs. Four oils are included: Macondo source, artificially weathered Macondo oil, and field collected Macondo weathered oil—Slick A and Slick B. The left column (A, C, and E) compares the filtered to the unfiltered TPAH50 concentration. The right column (B, D, and F) plots the ratio of unfiltered to filtered concentrations versus the unfiltered concentration. The WAFs are LEWAF and MEWAF (A, B), CEWAF (C and D), and HEWAF (E and F). For LEWAFs and MEWAFs, there is no difference between filtered and unfiltered TPAH50 concentrations, indicating that the microdroplet concentration is small relative to the dissolved concentration. However, for CEWAF and especially for HEWAF, the difference is large with the ratio of unfiltered to filtered TPAH50 concentration in HEWAF reaching two orders of magnitude for Macondo source oil. Note that the data form unity slope lines for HEWAF for each oil as the concentration of unfiltered TPAH50 increases, indicating that the dissolved TPAH50 concentrations are remaining constant and the increases are due to increases in microdroplet concentration.

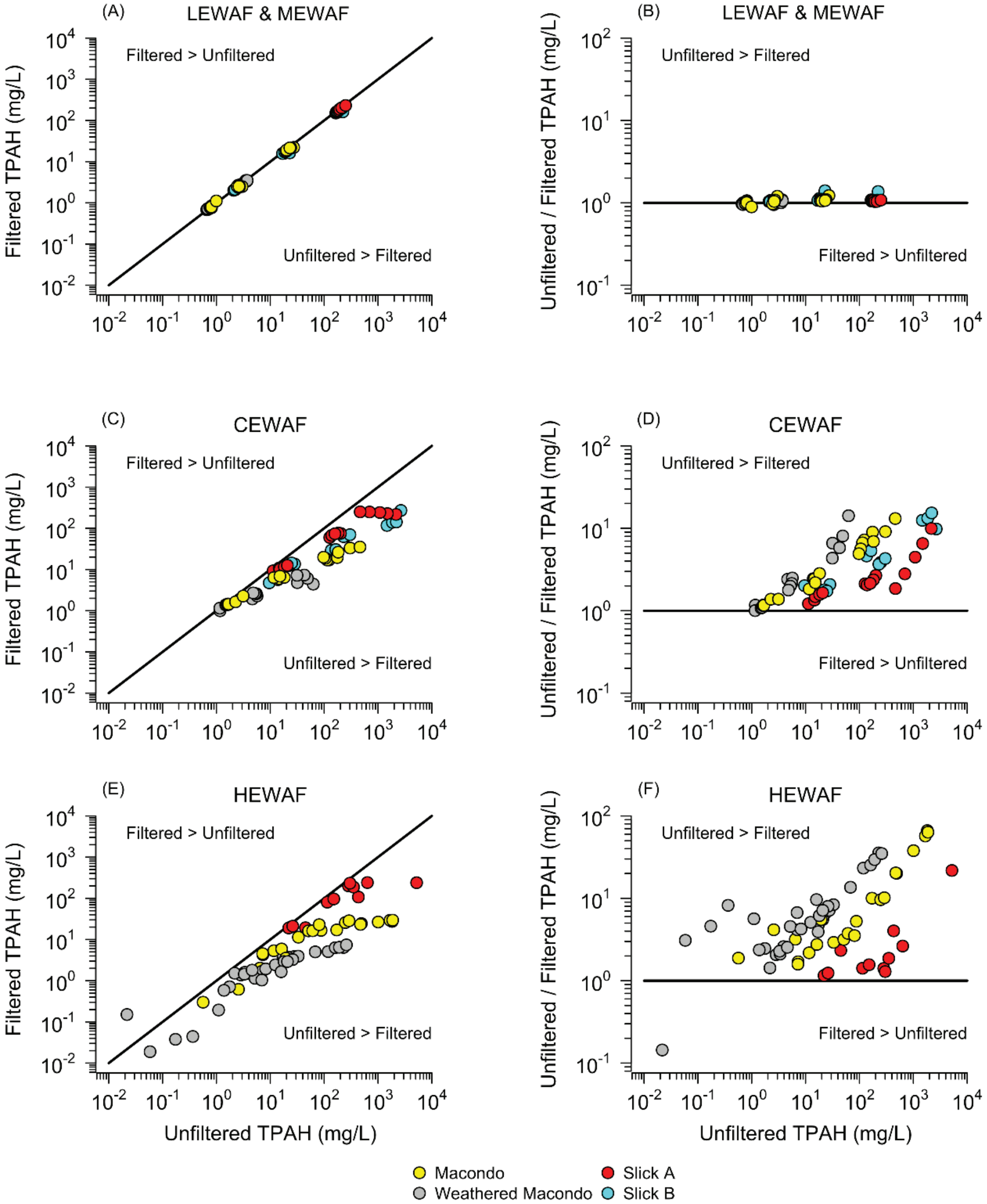

FIGURE 3.8 TPAH50 concentrations in LEWAFs/MEWAFs, CEWAFs, and HEWAFs. Left column (A, C, E): Measured TPAH50 concentrations in water samples with paired unfiltered (total concentration) and filtered (dissolved concentrations) TPAH chemistry. Right column (B, D, F): Ratio of unfiltered to filtered concentrations. First row (A, B): LEWAF and MEWAF; second row (C, D): CEWAF; third row (E, F): HEWAF. Colors indicate the oil: Macondo source, artificially weathered Macondo oil, field collected Macondo weathered oils: Slick A and Slick B. Lines represent equality of filtered and unfiltered concentrations. SOURCE: Data from DIVER, 2017.

These data indicate that the unfiltered total concentrations can differ from the filtered dissolved concentrations by one order of magnitude for CEWAFs and up to two orders of magnitude for HEWAFs. Because this ratio is varying widely, it is not possible to distinguish between the effects of dissolved components and microdroplets. Furthermore, PAH composition would also vary, further modulating toxicity, a point that is discussed in detail later in the chapter.

Variable loading tests directly address the question of whether the toxicity of physically and chemically dispersed oil differs. The comparison between the two is direct, because the dissolved concentrations at equilibrium are equal in both the LEWAF and the CEWAF for the same oil loading. The only difference is the amount and degree of aggregation of the undissolved droplet oil and the added exposure to dispersant. Thus, a comparison of LL50s derived using the variable loading method with and without dispersant allows the effect of dispersant on oil toxicity to be elucidated as illustrated previously in Figure 3.5.

As demonstrated above, interpretations based on total concentration, which include microdroplets, complicate the problem of understanding the toxicity of WAF versus CEWAF; the relationship between measured concentrations in the laboratory and field samples; and interpretations of observed toxicity. These and related conclusions (e.g., Redman and Parkerton, 2015; Sandoval et al., 2017) collectively emphasize the need to address the issue of microdroplets such that adequate interpretations of toxicity data may be made in the future. Estimation of toxicity values from variable dilution preparations should only be made based on analyses on filtered samples at each dilution and not solely on unfiltered samples in WAF stock, as is often the case for standard toxicity testing.

As an example of the difficulty of interpreting data, a study with early life stages of mahi-mahi found that the acute toxicity of CEWAF was higher than in HEWAF when comparisons were based on TPAH total concentrations, while their toxicities were comparable based on dissolved concentrations of TPAHs and 3-ring PAHs (Esbaugh et al., 2016). However, this study found higher lethality of weathered oil (Slick A) compared to source oil on the basis of either total or dissolved PAH, but not on the basis of dissolved 3-ring PAHs. These findings provide an example of how different metrics of toxicity could lead to divergent conclusions on the toxicity of different oils, pointing to the importance of hydrocarbon composition in the exposure media (see discussion on TUs below). These results are consistent with a test conducted with red drum embryos showing that cardiotoxic phenotypes of weathered oil prepared under LEWAF and HEWAF mixing energies were similar when expressed based on estimated dissolved TPAH concentrations (Morris et al., 2018).

The above discussions are not meant to suggest that oil microdroplets be removed from toxicity testing, as they may enhance the uptake of bioavailable PAHs through adhesion to outer embryo tissues (e.g., Carls et al., 2008; Redman et al., 2014; Sørhus et al., 2015). Instead, efforts should focus on understanding the influence of microdroplets on toxicity test results where the dissolved concentrations are measured and the appropriate TU dose metric is employed to quantify the toxicity of all the dissolved components. The additional toxicity, if any, can then be tentatively ascribed to the factors other than the dissolved concentrations, including microdroplets.

From an experimental point of view, the discussion above describes the practical advantages of the variable loading preparation method. An outstanding issue raised by the National Research Council (NRC, 2005) remains unresolved, however: namely, a conclusive demonstration of which method more appropriately simulates the complex time variable and compositional variation characteristic of conditions during a spill and spill response. While this question remains unanswered, an argument could be made that in order to allow laboratory to field extrapolations of toxicity data, predictive models would need to be employed. This could only be achieved, though, by using toxicity data from tests that address the issues introduced by the preparation method. A clear difference between the findings of the previous study (NRC, 2005) and this updated report is that empirical data are now available to support the technical basis of the variable loading method. This method produces data that can be used directly to answer the question whether exposure media containing chemically dispersed oil is more or less toxic than is exposure media containing physically dispersed oil. It can also be used to evaluate the performance of the available toxicity models that are used to predict toxic impacts in field exposures. Thus, the finding presented here may facilitate discussions toward consensus on a preferred preparation method among the scientific community. Given the different approaches used by various investigators (as discussed above) the benefits and limitations of various approaches are summarized in Table 3.1. This table provides an evaluation of various solution preparation methods, other exposure media preparations (e.g., contaminated sediments), the exposure regime/tempo, and options for quantifying the chemistry of toxic exposures.

MODELING THE TOXICITY OF OIL

In addition to its comparisons of media test preparation protocols, exposure durations, and chemistry approaches, the committee also considered the strengths and weaknesses of three approaches that have been used to quantify the toxicity of water-oil mixtures and arguments that have been made to support the use of TUs. The TU approach as advocated in this chapter implicitly assumes that (1) the toxic compounds can be identified; (2) their toxicity as individual compounds is known; and (3) if toxicity is then estimated, it is under a baseline minimal toxicity that does not account for the known specific mechanisms of PAHs and heterocyclic aromatics. All other dose metrics have the same requirements—that is, only the identified components with known concentrations can be added together into TPAH and TPH. Dose metrics based on known specific mechanisms need to be applicable to the evaluation of the toxicity of oil-water mixtures. A test of the utility of the target lipid model (TLM) and TUs for the prediction of chronic TUs has been published (Redman et al., 2017). A comparison of predicted and observed "no effect loadings" (Redman et al., 2017, Figure 5) and the observed dose responses versus chronic TUs (Redman et al., 2017, Figure 6) demonstrates the extent to which the TLM-TU model incorporated into PETROTOX correctly reproduces observed toxicity.

Understanding the toxicity of oil is complicated due to the nature of oil and its behavior in WAFs. The problems outlined above can only be addressed quantitatively using a model of the toxicity of oil that explicitly includes the processes that influence the distribution of components between the oil and aqueous phases and includes an appropriate aggregate dose metric that deals appropriately with the fact that individual components have widely differing toxicity. The next sections outline the present state of development of models of oil toxicity. The topics covered are

1. The toxicity of the individual petroleum hydrocarbons in an aqueous solution that make up the components of the oil;
2. The toxicity of a mixture of these compounds in an aqueous solution; and
3. The relationship between the oil composition and the dissolved aqueous concentrations of the compounds that results when oil and water mix.

Toxicity of Hydrocarbons

The aquatic toxicity of hydrocarbons has been studied extensively. They exert acute toxicity via a narcotic mode of action. Studies have reported the relationship between the toxicity of individual narcotic chemicals and their octanol-water partition coefficient K_{OW} (Di Toro et al., 2000; McGrath and Di Toro, 2009; Van Leeuwen et al., 1992; Veith et al., 1983). The TLM was developed to predict the toxicity of PAHs in particular and narcotic chemicals in general (Di Toro et al., 2000; McGrath and Di Toro, 2009). It is applicable to a wide variety of aquatic species with only one parameter required for each species. The TLM was initially calibrated using a large collection of mortality

TABLE 3.1 Benefits and Limitations of Various Methods for the Preparation of Water Accommodated Fractions (WAFs) and Other Media Preparation for Toxicity Testing of Oil in Water

Solution Preparation Protocols		Benefits	Limitations
LEWAF[a] Low-energy WAF	Deionized water added to aspirator bottle; stir bar set at 300 rpm to prevent any vortex[a]	Simulates passive dosing, method results in few dispersed droplets	May not account for realistic mixing energies, particularly resulting from a blowout
MEWAF Mid-energy WAF	Solution derived from vortex mixing (20%-25%) using magnetic stir bar with 18-24 hrs mixing and 2-8 hrs settlement period	Realistic mixing energies in terms of field-level extrapolation	Likely more variability in mixing in field applications than implied from laboratory protocol
HEWAF[a] High-energy WAF	Solution derived using the lowest speed with a food blender for a 30 sec blend and 1 hr settlement period	Results in dispersion of many (most) microdroplets	Unrealistic in terms of real-world mixing energies
SHEWAF[b,c] Super-high-energy WAF	Solution derived from the lowest blending speed using a food blender with 120 sec blend and 1 hr settle	Results in dispersion of many (most) microdroplets	Unrealistic in terms of real-world mixing energies
Variable dilution method	Solution derived from a single oil and water mixture (stock solution) from which dilutions are prepared	Standard stock solution prepared once at initiation of experiments	Dissolution of oil components from microdroplets results in changing concentrations of dissolved oil components
Variable loading method	Individual test solutions are prepared using variable concentrations (loadings) of oil	Multiple test solutions are prepared instead of one stock solution	This dissolved concentration is the same with and without dispersant added
Variable dispersant: oil ratios	Range of dispersant oil ratios used 1:10 to 1:100 dispersant-to-oil ratio to reflect both surface and subsurface use	Allows optimization of dispersant application	Subject to microdroplet induced changes in ratios if used with variable dilution method
Other Exposure Media Preparation		**Benefits**	**Limitations**
Oil emulsion[b]	Solution derived from a low blending speed using a food blender with 30 sec blend and used in its entirety without settlement	Allows interpretation of weathering oil	Complicated and rapidly changing weathering scenarios
Oiled sediment[b]	Sediments mixed with oil for 30 minutes at a moderate speed using either a large food preparation mixer or concrete mixer	Allows more complete interpretation of exposure vectors	Oiled sediments may be more layered than mixed laboratory preparations, subject to bioturbation and wave/current action in shallow waters
Sediment-derived WAF[b]	Supernatant derived by adding water to contaminated sediments then either stirring for 10 seconds followed by 2 hrs settle, or by shaking at 300 rpm for 6 hrs with 12 hrs settle	Simulates secondary water-based contamination from sedimented oil	Difficult to relate the cause of toxicity to oil composition and sediment properties

TABLE 3.1 Continued

Exposure Regime		Benefits	Limitations
Static renewal or nonrenewal	Refers to a constant exposure in which there is test solution renewal at regular time intervals (typically 24 hrs) with fresh test solution made at the same concentration or there is no test solution renewal	Constant exposure concentrations allow the construction of dose-response curves	Unrealistic assumptions of constant concentrations from actual oil spills
Co-stressors	Influence of co-stressors investigated (i.e., UV light, temperature, dissolved oxygen	Real-world oil exposures are complicated by these co-varying stressors that may be additive or multiplicative	Complicated to understand and requires factoral designs for experiments
Chemistry		Benefits	Limitations
Total PAH (TPAH or Σ50PAH) concentration	Arithmetic sum of PAHs, including alkyl homologues by GC/MS/SIM, individually quantified and generally comprised of 50+ PAH compounds (MC 252 QAPP, 2011)	Quantifies exposure to arguably the most toxic/carcinogenic constituents of oil	Does not weight the relative toxicity of various PAH compounds
Total petroleum hydrocarbon (TPH) concentration	Measures the total hydrocarbon concentration using a solvent extraction and quantification using 1-D GC-FID that typically sums from a lower cutoff up to typically C38 carbon number	Measures all TPH concentrations up to the very heavy components. If all the oil is measured before separation, this is equivalent to the oil loading.	No distinction between the variations in toxic components and additionally the highly weathered components that are not toxic
Chemical partitioning (dissolved/particulate phases)	Pass test solution through 2 stacked GF (0.3 µm) filters^{d,e,f} or glass wool and 1µm GF/F and 0.7 GF/F^{2} under gentle vacuum and analysis of filtrate and non-filtered test solutions	Removes dissolved droplets (depending on size) from test media thereby allowing interpretation of toxicity to dissolved oil	Microdroplets are a reality of oil spills and contribute to the overall exposure burden
Quantitation of droplets	Recommend analysis of size and distribution	Allows complete interpretation of oil in both droplet and dissolved manifestations	Difficult to understand the relative contributions of droplets and dissolved components in mixtures

NOTE: Modified from original table proposed by Mitchelmore et al., 2020.

[a] Bera et al., 2018.

[b] Krasnec et al., 2016.

[c] Sandoval et al., 2017.

[d] Carney et al., 2016.

[e] Forth et al., 2017a.

[f] Forth et al., 2017b.

data and subsequently has been extended to include a wider range of organisms from the initial 33 species to 79 species (McGrath et al., 2018). The TLM predictions of the acute LC50 data of single monoaromatic hydrocarbons (MAHs) and PAH compounds for various species are generally within a factor of 2 to 3 of the observed toxicity over a concentration range of approximately 10 µg/L to in excess of 100 mg/L (McGrath and Di Toro, 2009, Figure 1).

Chronic criteria based on sublethal endpoints have also been developed that protect the organism from a lifetime exposure (i.e., development as measured by growth and weight at maturity and reproductive success). The parameter that has been used historically to estimate the chronic criteria is the acute-to-chronic ratio (ACR; Stephen et al., 1985). The chronic criteria are computed by dividing the acute criteria by the ACR. Following this approach, ACRs for individual petroleum hydrocarbons have been developed, resulting in a probability distribution of species geometric average ACRs (McGrath et al., 2018). These updated ACRs facilitate extrapolation of acute to chronic toxicity values.

Modern chronic criteria, first utilized by the European regulatory agencies, are based on the HC5 concentration (Aldenberg and Slob, 1993), which is established by treating the variations in species sensitivity and the ACR as probability distributions and computing the concentration that protects 95% of the tested species. The use of the probability distributions of both the SSD and the ACR accounts for the variation in the SSD and the ACR for the tested species. Based on the updated ACRs, chronic TLM-derived HC5s for baseline narcotics, MAHs, and PAHs were developed, confirming that these values are protective of species for which chronic data are available (McGrath et al., 2018).

Toxicity of Mixtures: Toxic Units

The soluble oil components contribute to aquatic toxicity to variable degrees, and a model is needed to quantify the toxicity of mixtures. For components that exert their toxicity through a narcotic mode of action, the use of TUs has been shown to correctly predict observed toxicities (Hermens, 1989).

The TU concentration for a specific compound is defined as the ratio of the dissolved aqueous concentration of the compound, C_W, to the toxic concentration, either *LC50* or *HC5* of that compound, as shown in Equation 1.

$$TU = \frac{C_W}{LC50} \tag{1}$$

For a mixture of N compounds with concentrations $C_{W,1}$, $C_{W,2}$, …, $C_{W,N}$, the predicted TU concentration for the mixture TU_T is the sum of the individual TU concentrations, as shown in Equation 2.

$$TU_T = \frac{C_{W,1}}{LC50_1} + \frac{C_{W,2}}{LC50_2} + \ldots + \frac{C_{W,N}}{LC50_N} \tag{2}$$

If the total TU concentration $TU_T = 1$, the mixture is predicted to cause a 50% effect if LC50s are used for the effect concentration in Equations 1 or 2. Equation 2 has been validated using data from a number of studies, using mixtures of up to 50 compounds (Hermens, 1989). The toxicity of mixtures of PAHs has also been tested, and the predictions based on TU additivity have been shown to be within the usual range of a factor of two or three, consistent with single chemical toxicity predictions (Di Toro and McGrath, 2000; McGrath et al., 2005; Redman et al., 2012b).

Modeling the Toxicity of Oil—PETROTOX

The PETROTOX model has been developed to predict the aquatic toxicity of water in contact with oil (Redman et al., 2012b). It uses the TLM to predict the toxicity of the individual oil components and the TU mixture model to predict the toxicity of the mixture. An earlier model Oiltox (French-McCay, 2002) also used the TLM and TUs as the basis for predicting the toxicity.

PETROTOX is comprised of four parts:

1. The composition of the oil being evaluated is specified as a mixture of a number of blocks. For each block, a chemical is selected whose physical and chemical properties are similar to the concentration of the chemicals found in that block. This block approximation is designed to be compatible with the two-dimensional gas chromatographic (GC×GC) method that is used to quantify the composition of the oil (Reddy et al., 2012). For the Macondo oil, there are 318 non-zero block concentrations that comprise the input. PETROTOX includes both a high and a low resolution blocking scheme (e.g., aromatic versus aliphatic), which makes it applicable to a lower resolution analysis of the oil.
2. The model for the WAF determines the dissolved concentrations using Raoult's Law and the composition of the oil phase. The equilibrium composition is computed for both the oil and the aqueous phase (Di Toro et al., 2007).
3. The TLM is used to compute the LC50 for acute toxicity or for chronic toxicity using the ACR, as described above, for each of the dissolved concentrations.
4. The TU model (Equation 2) adds the TUs to produce the total TU_T for that oil.

PETROTOX predictions have been compared to experimentally determined toxicity of various oil samples using LL50 concentrations obtained from variable loading tests (Redman et al., 2017). The types of petroleum products that have been tested are naphtha, kerosene, gas oils, heavy fuel oils, distillate aromatic extracts, residual aromatic extracts, and other residual classes. Organisms tested are fish, zooplankton, and algae. The algae and daphnia predictions are generally within a factor of three. The predicted LL50 for fish is smaller than the observed LL50. This has been attributed to the loss of dissolved hydrocarbons during the test procedures (Redman et al., 2017).

PETROTOX is used below to:

1. Predict the toxicity of various oils;
2. Examine the utility of TPH and TPAH as dose metrics for the mixture of petroleum components in WAFs; and
3. Evaluate how the toxicities of different oils vary with oil loading and microdroplet concentrations.

Toxicity of Various Oils

PETROTOX can be used to predict the toxicity of oils for which the detailed oil composition obtained by using the comprehensive GC×GC method is available (Reddy et al., 2012). The required acute and chronic HC5 critical body burden required for the calculation are from McGrath et al. (2018). Figure 3.9 presents the toxicity of 10 oils, ranging from fresh to highly weathered samples. The acute HC5s TUs of the WAFs are plotted against oil loading. At the highest loading (1,000 mg oil/L), the WAFs of the least toxic oils—for example, Macondo Slick A and Slick B—are saturated

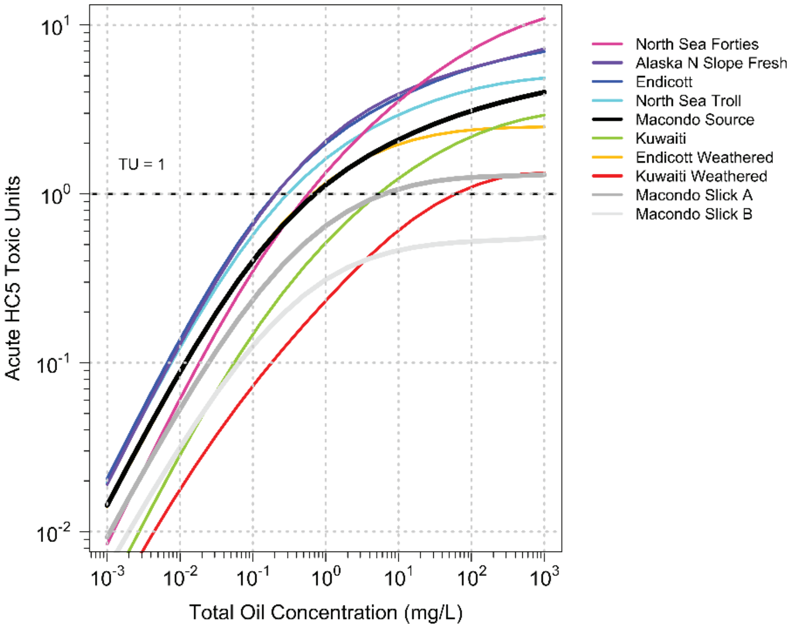

FIGURE 3.9 Acute HC5 toxic units (TUs) versus oil concentrations (mg oil/L) for 10 oils. Dashed line at TU = 1. Oils are sorted by TU at the total oil concentration = 10^3 (mg/L). The acute HC5 concentrations are computed using PETROTOX predictions for oils with available detailed oil compositions. The TUs are based on dissolved concentrations. The acute HC5 critical body burden required for the calculation is from McGrath et al., 2018.

and have reached their highest toxicity, whereas the toxicity of the WAFs of the most toxic oils (e.g., North Sea Forties) would increase at higher loadings, as indicated by the upward curves of the lines. As the oil loading decreases the acute HC5 TU concentrations—and therefore the toxicity—all decrease, but not in proportion to the reduction in loading until the loadings decrease below approximately 1.0 mg oil/L. There are significant differences among the oils between the rate of decline and the toxicity. Slick B oil, the most weathered, never reaches a level of TU = 1. At TU = 1, the loading for the various oils ranges from approximately 100 mg oil/L to nearly 0.1 mg oil/L, a difference of almost three orders of magnitude. This shows that there are significant differences due to the oil composition, and that for the same oil (e.g., Macondo, Endicott), toxicity decreases with weathering. Therefore, if toxicity predictions are required to be representative of a specific fresh or weathered oil, its composition must be known or approximated by an oil of known composition.

Dose Metrics: Toxic Unit, TPH, and TPAH

In order to quantify the toxicity of a mixture, a dose metric is necessary to establish the dose response. As discussed above, the dose metric for mixtures of the hydrocarbons in oil that correctly predicts the observed dose response in many experiments is the TU (see Equation 2). Unfortunately, this is not the metric that is normally used in either toxicity tests or in reporting field observations. The most common dose metric is TPAH, which is the arithmetic sum of the concentrations in weight units (e.g., µg TPAH/L). A more complete sum is TPH that includes all the hydrocarbons that are resolved using the analytical method employed. Equations 3 and 4 define TPAH and TPH, respectively. A comparison to the defining equation for TUs (Equation 2) illustrates the differences in these dose metrics.

$$TU_T = \frac{C_{W,1}}{LC50_1} + \frac{C_{W,2}}{LC50_2} + \ldots + \frac{C_{W,N}}{LC50_N} \tag{2}$$

$$TPAH = PAH_1 + PAH_2 + \ldots + PAH_N \tag{3}$$

$$TPH = HC_1 + HC_2 + \ldots + HC_N \tag{4}$$

The TU_T (Equation 2) weights the concentration of each petroleum hydrocarbon C_W by its effect concentration *LC50*, using the dissolved concentrations. *TPAH* (Equation 3) and (Equation 4) are the sums of the aqueous concentrations without regard to their individual toxicity, and they are usually the sum of the dissolved and microdroplets concentrations. In addition, TPAH only considers the PAHs in the mixture.

It is clear from Equations 2-4 that these three dose metrics are incompatible if they are used to compare oils of differing composition. Consider the example presented in Table 3.2. Two example oils, labeled "Neat" and "Weathered," are assumed to be composed of equitoxic mixtures of the PAHs listed. The neat and weathered oil composition results in one TU. Therefore, both oils result in 50% mortality and are equally toxic. The TPAH concentrations, however, are different because the two least toxic PAHs with the highest concentrations are not in the weathered oil. Therefore, if only the TPAH concentrations were used as the dose metric, the weathered oil has a lower TPAH concentration at 50% mortality (TPAH LC50 = 14.4 µg/L) than does the neat oil (TPAH LC50 = 49.4 µg/L) and therefore would be judged to be the more toxic oil. Using the TU dose metric, both of these oils would be judged to be equitoxic. This problem has been addressed in an investigation of the relative toxicity of neat and weathered oils. It demonstrates that the use of TPAH leads to the incorrect conclusion that weathered oils are more toxic than neat oil is (Di Toro et al., 2007). What follows is a more detailed evaluation that uses the PETROTOX model to examine the extent that TPAH values correlate to TUs, and it can therefore be used as a surrogate for TUs.

TPAH and TPH can be used if the fractional composition of the dissolved components in the aqueous phase is not changing. For this situation, the TPAH and TPH would be proportional to the TU concentrations. Note that for cases where the dissolved concentrations of the TPAH and TPH are explicitly measured, the computation of the TU concentration is straightforward because the acute LC50 and chronic EC20 are available for many species (Di Toro and McGrath, 2000; Di Toro et al., 2000; McGrath et al., 2004), and the acute and chronic HC5s are also available if the species of interest is not available (McGrath et al., 2018).

Another problem with TPAH is that it does not capture all the toxic components. The comparison below considers the toxicity of an aqueous phase WAF in equilibrium with a large enough oil loading to ensure that the oil composition is not significantly altered by the dissolution of the oil components into the aqueous phase once equilibrium has been achieved. The resulting saturated aqueous phase has the highest dissolved concentrations that can exist for this oil. Figure 3.10 presents the results of a PETROTOX simulation for the 10 oil samples presented in Figure 3.9, for which the detailed composition is available at an oil loading = 10 g oil/L that saturates the aqueous phase. The figure presents both the sum of the acute HC5 TUs due to dissolved PAHs only and the total TU that considers all the dissolved hydrocarbons.

The results indicate that acute HC5 TU concentrations for saturated WAFs vary from ~5 to ~50 TUs, whereas the TUs due to total PAHs vary from ~1 to ~10 TUs. It is clear that for several of the oils, the PAHs are not the major source of TUs and, therefore, the toxicity of the WAF. Therefore, using TPAH as a dose metric would miss a significant fraction of the toxic components for the

TABLE 3.2 Comparison of Total PAH and Toxic Unit Dose Metrics

Neat Oil					
Chemical	log Kow	HC5 (uM)	HC5 (ug/L)	EqiTox (ug/L)	EqiTox (TU)
Naphthalene	3.256	1.033	132	22.000	0.167
Acenaphthylene	3.436	0.7	107	17.833	0.167
Acenaphthene	3.878	0.269	41.5	6.917	0.167
Anthracene	4.546	0.0633	11.3	1.883	0.167
Pyrene	5.126	0.018	3.64	0.607	0.167
Chrysene	5.782	0.00434	0.99	0.165	0.167
				TPAH	TU
			Sum	49.405	1.000
Weathered Oil					
Chemical	log Kow	HC5 (uM)	HC5 (ug/L)	EqiTox (ug/L)	EqiTox (TU)
Acenaphthene	3.878	0.269	41.5	10.375	0.250
Anthracene	4.546	0.0633	11.3	2.825	0.250
Pyrene	5.126	0.018	3.64	0.910	0.250
Chrysene	5.782	0.00434	0.99	0.248	0.250
				TPAH	TU
			Sum	14.358	1.000

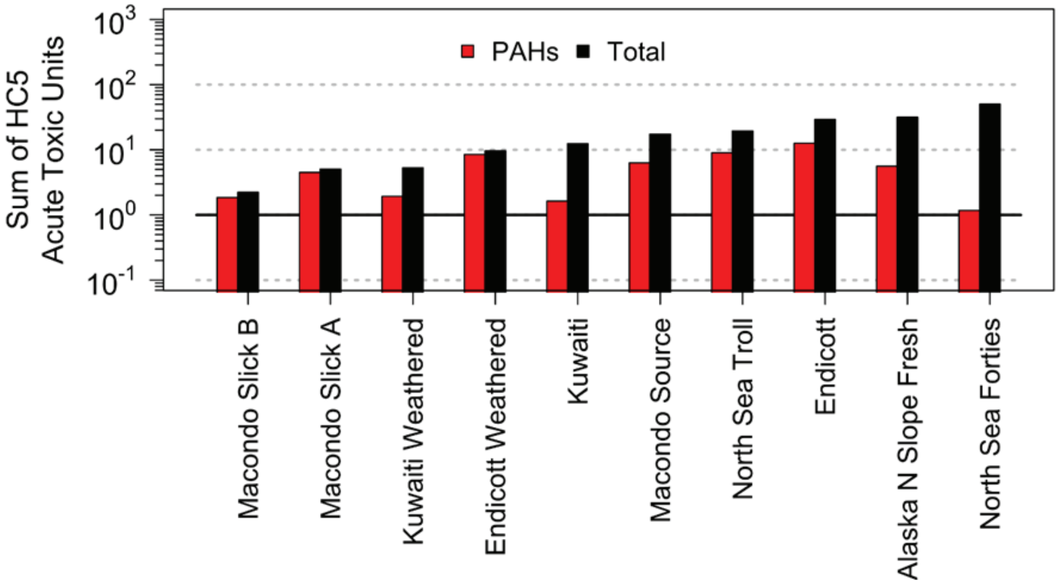

FIGURE 3.10 The total acute HC5 TU concentrations TU_T, and the TU concentrations of the TPAH components for saturated WAF, computed at total oil loading = 10 g/L. The TUs are computed using the HC5 species sensitivity for acute mortality (McGrath et al., 2018). The horizontal line is at 10^0 = 1 TU.

majority of these oils, in addition to not having the appropriate normalization that is included in derivation of TUs (Equation 1). For these two reasons, the use of TPAH as a dose metric is not scientifically defensible when applied across oils or different weathering states of the same oil.

Effect of Variable Oil Concentrations

The previous section examined the toxicity of oil of a saturated WAF. In this section, the toxicity of Macondo oil is computed as it is diluted from oil loadings that produce a saturated WAF (10^4 mg oil/L) to a very diluted concentration of 10^{-3} mg oil/L = 1 µg oil/L. Figure 3.11A shows the resulting TPH and TPAH dissolved concentrations as well as the concentration of undissolved remaining oil.

Even at the lowest total oil concentration (1 µg oil/L), a liquid oil phase (“remaining oil”) persists because not all the oil components are soluble. As the amount of added oil increases, both TPH and TPAH start to approach the saturated concentrations.

Figure 3.11B presents the acute HC5 TUs due to PAHs (TPAH-TU) and the total acute HC5 TU concentrations versus oil concentration. The dashed line is a unity slope line. At low oil concentrations of 1 to 10 µg oil/L, the increase in TU concentration is almost in proportion to the increase in loading concentrations (compare to the unity slope line). However, at higher concentrations, both the TU and the TPAH-TU curves begin to plateau as the samples approach saturation. As saturation is approached, the TU and TPAH-TU curves start to diverge, indicating that the TPAH-TUs represent an increasingly smaller fraction of the total TUs present in the mixture.

In practice, the concentrations of TPH and TPAH are used as dose metrics. Their validity and utility can be judged by comparing TPH and TPAH concentrations to the TU concentrations as a ratio. If the TPH and TPAH are proportional to TUs then these concentrations can serve as dose metrics that are proportional to the TU concentration. Figure 3.12 presents the results.

At low total oil concentrations (i.e., < 10 µg/L = 10^{-2} mg/L), both TPH/TU and TPAH/TU ratios are reasonably constant and therefore can be used as dose metrics for this oil. However, as the oil concentration increases, the ratios start to increase. For TPH and TPAH, the ratios climb by approximately two and 1.5 orders of magnitude, respectively, as saturation is approached. Therefore, for total oil concentrations of > 100 µg/L = 10^{-1} mg/L, TPH and TPAH are no longer representative of the TU concentration. They are not a constant multiple of the actual TU concentration. Their use as dose metrics for toxicity tests at different total oil concentrations can lead to incorrect

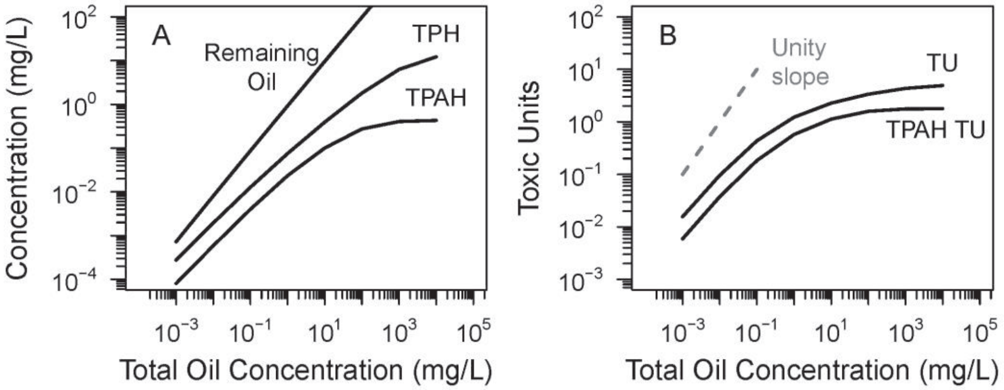

FIGURE 3.11 (A) Concentrations of total PAH (TPAH), total petroleum hydrocarbons (TPH), and remaining undissolved oil. (B) TU concentrations of the TPAHs (TPAH TU) and total TUs. The dashed line has unity slope for visual comparison.

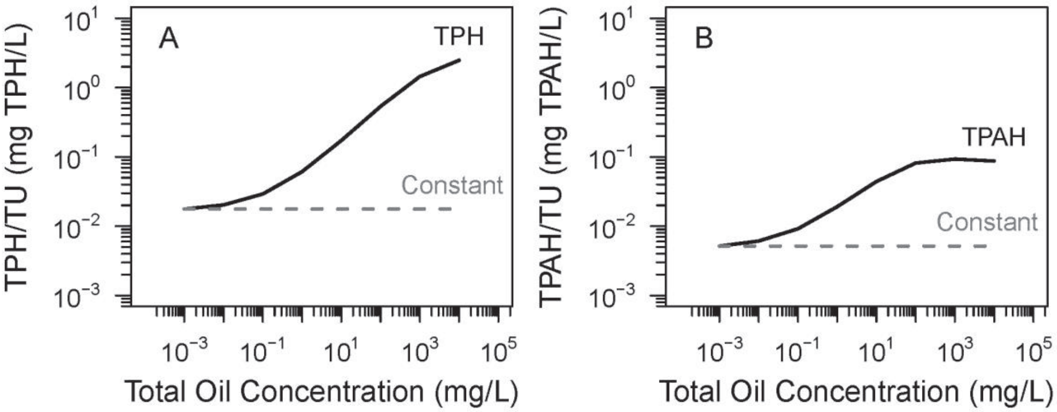

FIGURE 3.12 Ratio of TPH (A) and TPAH (B) concentrations to TU concentrations. Concentrations from Figure 3.11. NOTE: The dashed line denotes a constant ratio.

conclusions. Also, because these ratios change with different oils, using TPH and TPAH as a dose metric to compare the toxicity of different oils would likely be misleading. Unfortunately, this is the range at which most toxicity tests are conducted, as seen in the results of PETROTOX simulations of the TU concentrations of the 10 oils examined in Figure 3.9.

Concentration of Microdroplets

The previous sections analyzed the behavior of the dissolved concentrations in an oil-water mixture. This section examines the effects of the presence of microdroplets in the WAF.

There is a large variation in the concentration of droplets in various WAFs, which is the result of varying mixing energies and the use of dispersants. A recent report (Forth et al., 2017b) examined the LEWAF, CEWAF, and HEWAF prepared from four oils collected from the DWH oil spill. Figure 3.13 presents the percent dissolved in the three WAFs.

In LEWAF preparations, the percent dissolved PAH concentrations comprise the large majority (> 90%) of the total dissolved oil concentrations resulting from the minimization of oil droplet interference by mixing the exposure media without promoting microdroplet formations. In contrast, the percent dissolved for CEWAF and HEWAF are a smaller percentage of the total dissolved concentrations (below ~20% and ~5%, respectively), indicating that the majority of the oil in these dispersed WAFs is not dissolved. This is a critical issue because these concentrations are usually incorrectly assumed to be bioavailable. Therefore, a careful consideration of the effect of the microdroplets on the dissolved concentrations and toxicity is required.

The concentration of microdroplets is difficult to measure directly, but it can be inferred from the measured concentration of essentially insoluble components of the oil (Redman et al., 2012a).

PETROTOX is used to predict the concentration of dissolved oil and the composition of the remaining oil phase that is expected to be present for an oil of known composition and concentration in the WAF. The concentration of microdroplets is estimated to reproduce the measured concentrations. For the cases investigated, the concentration of microdroplets ranged from ~50 to ~500 µg oil/L (Redman et al., 2012a).

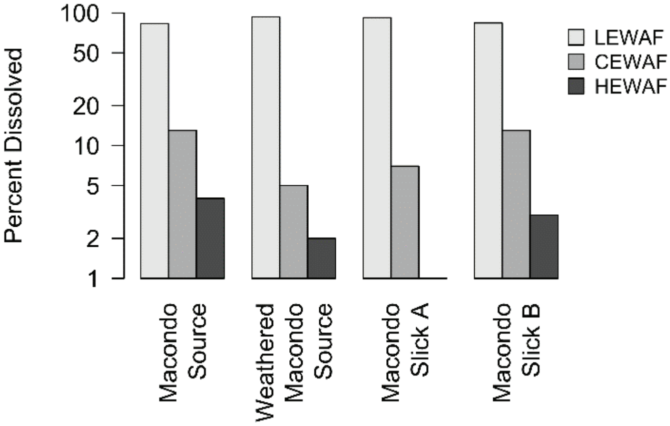

FIGURE 3.13 Percentage of the total oil concentration in the WAF that is dissolved. Comparisons of four oils: Macondo, Weathered Macondo, Macondo Slick A, and Macondo Slick B. Weathered Macondo is artificially weathered Macondo, whereas Macondo Slick A and Macondo Slick B are heavily weathered samples collected from the field. Three WAF types are included: low-energy mixing LEWAF, chemically enhanced CEWAF, and high-energy mixing HEWAF. The dissolved concentrations are the same as are presented in Figure 3.4. SOURCE: Data from Forth et al., 2017b.

Effect of Microdroplets on Dissolved Concentrations in Variable Dilution Media

The failure of the variable dilution toxicity test to determine whether the addition of dispersant increased or decreased the toxicity of the exposure media containing oil (as shown in Figure 3.7) is attributed to the influence of microdroplets. The magnitude of the departure from the concentration estimates using dilution is remarkably large (as shown in Figure 3.14), a PETROTOX simulation of a variable dilution experiment.

Without microdroplets (dashed line) the TPH concentration (see Figure 3.14A) decreases linearly with dilution: for instance, a 10-fold decrease in TPH for a 10-fold decrease in total oil, corresponding to a 10-fold dilution. For small microdroplet concentrations = 1.0 and 10.0 μg/L (red and green lines), the decrease is almost linear, although there is a contribution to the TPH concentration from the dissolution of the microdroplets. At higher midrodroplet concentrations = 100 and 1,000 μg/L (blue and black lines), the contribution of microdroplet dissolution is substantial, causing an increase in excess of one order of magnitude. Recall that the range in microdroplet concentrations found in LEWAF toxicity tests ranged from ~50 to ~500 μg/L.

The contribution of microdroplets dissolution to acute HC5 TUs (see Figure 3.14b) is even more extreme. The dilution to achieve TU = 1 varies as the microdroplet concentration (MD) increases. For MD = 0 the dilution D_0 = 0.133. For microdroplet concentrations of MD = 1, 10, and 100 μg/L the dilutions at TU =1 are D = 0.071, 0.016, and 0.0018. The problem with using a variable dilution toxicity test to determine whether adding dispersants increases toxicity is that the dissolution of microdoplets increases the toxicity dramatically. There may or may not be additional toxicity due to the dispersant, but the effect of microdroplet dissolution is so large that the additional toxicity may not be detected.

The flaw with the variable dilution test design is that dilution is used as a surrogate for the dose metric, and in the presence of microdroplets, the actual TUs in the aqueous phase will vary systematically for a *given* oil type, but not *among* oils, thereby hindering comparisons across multiple studies (e.g., meta-analyses). It is for this reason that variable loading tests are

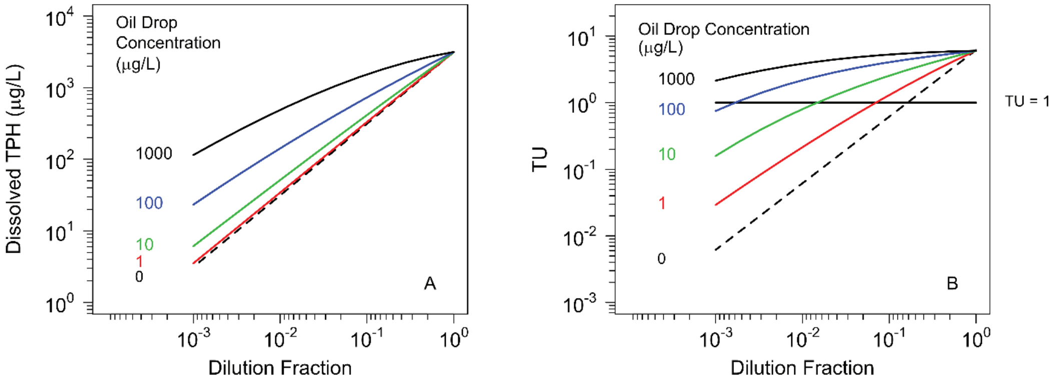

FIGURE 3.14 Dissolved TPH and acute HC5 TU concentrations that result from the dissolution of microdroplets. The concentration of microdroplets ranges from no microdroplets (dashed line) and from 1 to 1,000 μg oil/L. The x axis is the dilution fraction.

the recommended test design (e.g., OEDC, 2002) for evaluating the effect of dispersant on the toxicity of oil. The dose metric is unambiguous: that is, the concentration of oil added to the aqueous phase. The quantity of oil actually added needs to be verified by measurement such as a comprehensive TPH measurement that includes all the oil in the sample (see Table 3.1). Tests reporting only nominal oil concentrations are not acceptable.

Effect of Exposure Time

Exposure time, the duration of time that the organism is exposed to the chemical, is important in determining the effect of that exposure. The progressive decrease in the 24-hour, 48-hour, and 96-hour LC50 concentrations commonly found attests to the usual finding that increasing the length of exposure results in higher lethality for a given concentration. The designation of acute versus chronic toxicity testing differentiates between shorter and longer exposure times.

The variations in exposure times and concentrations can be extreme during oil spills. Therefore, an understanding of the effect of exposure time is an important component in determining the effect. The French-McCay OilToxEx model (French-McCay, 2002) includes a consideration of the effect of exposure time (see Equation 5):

$$\ln(LC50) = \ln(LC50\infty) - (\ln(1 - e^{-a}) \tag{5}$$

where is the LC50 as t → ∞ and ϵ is the elimination rate constant. $\ln\left(\epsilon\right)$ is a decreasing function of log K_{OW} and an increasing function of temperature. A more recent analysis examined the effect of organism life history characteristics and found large species-specific differences for ϵ. For fish, however, ϵ is slightly dependent on log K_{OW}, and for invertebrates ϵ is invariant with respect to organism weight, temperature, and log K_{OW} (Redman, 2018). A comparison of these two models is presented in Figure 3.15 for four PAHs.

Both models behave similarly. There is a dramatic variation in toxicity for exposure times less than or greater than 24 hours. As a point of reference, under noncontinuous oil releases in the open ocean, both physically and chemically dispersed oil are subject to rapid dilution, resulting in concentrations declining rapidly over time, typically within 4 hours (reviewed in Bejarano et al., 2014b). The horizontal lines in Figure 3.15 are the aqueous solubility of the compounds. If the

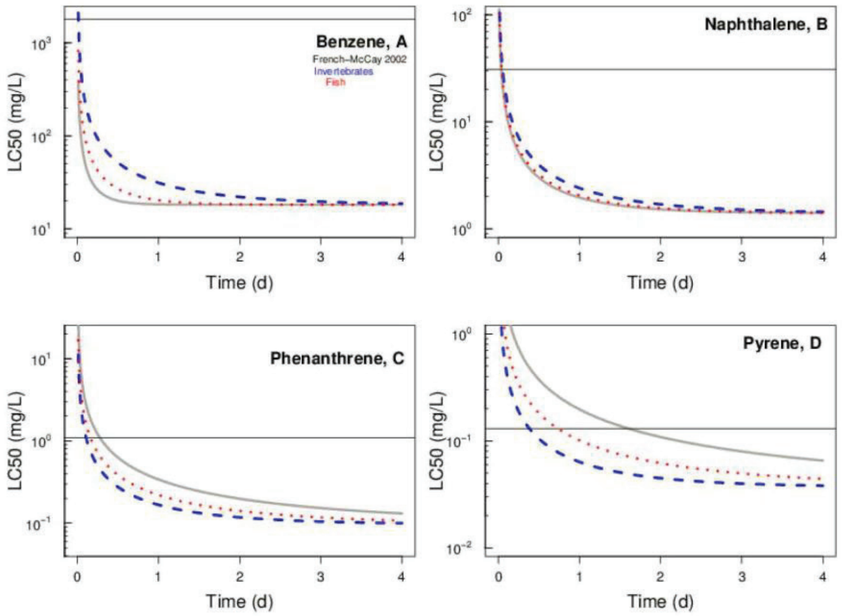

FIGURE 3.15 Variation of LC50 versus time of exposure (Redman, 2018). Compounds: benzene (A), naphthalene (B), phenanthrene (C), and pyrene (D). Exposure to invertebrates (blue dashed line), fish (red dotted line). Solid line: Model proposed by French-McCay (2002). Solid horizontal line, aqueous solubility. No toxicity is predicted for time where the LC50s exceed aqueous solubility. SOURCE: Redman, 2018.

model LC50 exceeds the aqueous solubility, the prediction would be that no mortality is observed for that duration of exposure. It is clear that the effect of exposure time is a necessary component of evaluating the toxicity in field situations where the patchy distribution of the oil results in variable durations of exposure. Toxicity tests that are designed to augment the available data for shorter exposure periods could be used to estimate HC5s for exposure times less than the available 96-hour HC5.

Phototoxicity

The fact that exposure to solar radiation increases the toxicity of certain PAHs in mammalian species has been known for more than 80 years (Findlay, 1928). For aquatic species, comprehensive reviews are available (Arfsten et al., 1996; Barron, 2017; Diamond, 2003; Giesy et al., 2013), and a mechanistic explanation of the phototoxicity pathway is provided in the previous NRC report (NRC, 2005). Briefly, the mechanism is referred to as photosensitization. The PAHs that partition into the organism absorb light energy and are converted to an excited state that decays and causes tissue damage within the organism (Little et al., 2000).

Exposure to ultraviolet also causes PAHs to photodegrade. The extent of photo degradation and the toxicity of the photodegradation products need to be considered as well. The research in this area has focused mainly on photodegradation (Bacosa et al., 2015; Huba et al., 2016; Maki et al., 2001; Shankar et al., 2015; Vergeynst et al., 2019). Determining the toxicity of the degradation products may require a more advanced model than the TLM for the narcosis mode of action as discussed below.

An example of the increase in toxicity of four PAHs to *Daphnia magna* exposed to simulated solar radiation is shown in Figure 3.16A, which presents the LC50s in the absence and presence of simulated sunlight.

For certain PAHs with a large overlap of the absorbance and solar radiation spectrum (fluoranthane and anthracene), the increase in toxicity can approach 100-fold. For other PAHs, the increase is less: for example, chrysene increases by a factor of 10. For other compounds, such as phenanthrene, there is no observed increase. It is interesting to note that while anthracene and phenanthrene are at the opposite end of the degree of phototoxicity, they are isomers with the same number (3) of aromatic rings as well as the same toxicity in the absence of solar radiation. The different molecular structure, namely, how the rings are fused, is responsible for the difference in the absorbance spectra and the consequent remarkable difference in phototoxicity.

In order to be able to predict the toxicity of a WAF, it is necessary to predict the phototoxicity of each component. A number of models of PAH phototoxicity have been proposed. Table 3.3 presents the models and the mechanisms that are included in the formulations. The models consider, in varying degrees, the absorbance spectra of PAHs, the spectral distribution of the incident radiation, the length of time of exposure, and the sensitivity of the species in question.

A model that addresses each of these processes is the Phototoxic Target Lipid Model (Marzooghi et al., 2017), which is based on the TLM used in PETROTOX. It computes the ratio of the phototoxic LC50 (PLC50) to the TLM LC50 as a function of the spectral absorbance of the PAH and the spectral distribution of the incident light exposure. The model has two constants that apply to all PAHs and organisms. It has been calibrated using the acute mortality LC50s and also the lethal time to death (LT50), the length of time of exposure required to cause 50% mortality at a specific concentration. The calibration dataset consists of 333 observations for 20 individual PAHs and 15 test species that include arthropods, fishes, amphibians, annelids, mollusks, and algae. The exposures are simulated solar and various UV light sources. The exposure times vary from less than 1 hour to 100 hours. The resulting LC50 concentrations range from less than 0.1 μg/L to greater that 10 mg/L. The root mean square errors of prediction for log (LC50) and log (LT50) are 0.473 and 0.382, respectively.

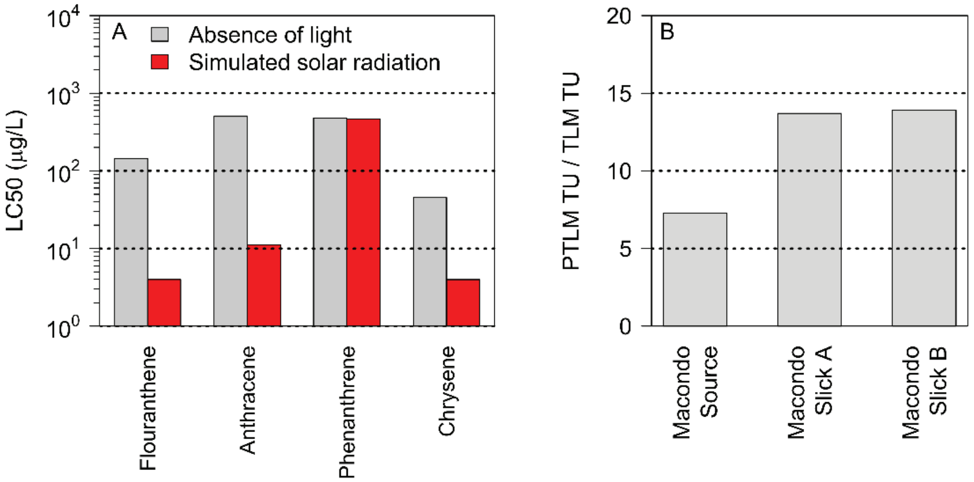

FIGURE 3.16 (A) Increase in toxicity to *Daphnia magna* due to simulated sunlight absorption for four PAHs: fluoranthene, anthracene, phenanthrene, and chrysene (Lampi et al., 2007). (B) Predicted ratio of phototoxic TUs to TLM TUs for three oils: Macondo Source, Slick A, and Slick B at saturated concentration. Exposure is to simulated sunlight (Marzooghi et al., 2018). SOURCES: Lampi et al., 2007; Marzooghi et al., 2018.

TABLE 3.3 Characteristics of Available Phototoxicity Models

PAH Phototoxicity Model	PAH Absorbance Spectra Used	Incidence Light Spectra	Duration of Light Exposure Used	Quantity Predicted	BCF Used	Method to Deal with Species Sensitivity[a]	Method to Deal with Chemical Potency[b]	Number of PAHs Considered	Number of Species Considered
Morgan and Warshawsky, 1977	√	UV 366 nm	√	ANI[c] Rate	√		RPA[g]	28	1
Newsted and Giesy, 1987	√	UV	√	QSAR[c]	√		RPA[g]	20	1
Mekenyan et al., 1994		UV		QSAR[d]			HOMO-LUMO gap	20	1
Oris and Giesy, 1985		UV	√	LT50				1	1
Ankley et al., 1995		UVA	√	LT50	√			3[i]	1
Krylov et al., 1997	√	UV+VIS		QSAR[e]				16	1
Grote et al., 2005a	√	UV+VIS	√	LC50	√		RPE[h]	11	1
Sellin Jeffries et al., 2013		UVA	√	LT50		RPA[f]	RPA[f]	18	4
Marzooghi et al., 2016	√	UV+VIS	√	LC50 and LT50	√	TLM Critical Lipid Conc.	TLM Lipid-H2O Partition Coef.	20	15

NOTE: ANI = average number of Artemia salina nauplii immobilized; HOMO-LUMO gap = difference in energy between the highest occupied molecular orbital and the lowest unoccupied molecular orbital; LC50 = lethal concentration at 50% mortality; LT50 = lethal time at 50% mortality; RPA = relative phototoxic activity; UV = ultraviolet; VIS = visible.

[a] Factor accounting for the difference between organism sensitivities.

[b] Chemical toxicity potency accounting for differing chemicals properties.

[c] Quantitative structure–activity relationship (QSAR) model developed to predict the LT50 using the empirical physiochemical parameters.

[d] QSAR to predict LT50 based on HOMO-LUMO gap.

[e] QSAR to calculate photosensitization constant and a photomodification constant.

[f] Relative phototoxic activity (RPA) = (LT50PAHi)1/(LT50Anthracene)1.

[g] Potency (rate of mortality per unit time per unit of absorbed irradiance) relative to that of the reference compound (benzo[b]anthracene).

[h] Relative phototoxic efficacy calculated as coefficients for each PAH.

[i] Regression analyses for each PAH separately. Chemical potency correction not performed.

SOURCE: Adopted from Marzooghi and Di Toro, 2017.

The Phototoxic Target Lipid Model has been validated by predicting the PLC50s for four species exposed to artificial sunlight for 12 compounds, including alkylated PAHs and dibenzothiophene in single compound tests, and for binary and ternary mixtures of pyrene, anthracene, and fluoranthene using TU addition as the mixture model (Marzooghi et al., 2018). It uses the same framework as the TLM to compute the TU concentration. Using this framework, the Phototoxic Target Lipid Model was used to predict the toxicity of WAFs of neat and naturally weathered Macondo crude oil samples (Source, Slick A, and Slick B) to three Gulf of Mexico species. The root mean square errors of prediction were comparable to the calibration dataset.

The predicted increase in phototoxicity for each of the three Macondo oils, a factor of approximately 6 to approximately 14, is presented in Figure 3.16B as the ratio of phototoxic PAH TU to narcotic PAH TU at saturation. The weathered oils exhibit the largest increase, which is due to the larger percentages of phototoxic PAHs in the weathered oils. This would increase their toxicity so that more weathered Slick A would be approximately as toxic as the fresher Macondo source oil (see Figure 3.9). This result also indicates that a comprehensive model is required for the prediction of the toxicity in the presence of solar radiation.

The use of dispersants can affect the concentration and composition of the oil that rises to the surface where solar radiation can increase toxicity. A number of factors need to be considered. For an application of dispersant to a surface spill, the dispersant would increase the dissolved concentrations. The dispersed oil droplets would be mixed into the top few meters, and PAHs would dissolve from the droplets to increase the aqueous concentrations. Oil droplets may also reduce UV attenuation in the water column, potentially reducing phototoxicity. Thus, while the volume of water potential impacted by photoxicity may be increased in the presence of surface dispersant application, the resulting risks are unclear.

For the subsea dispersant injection, the reduction in droplet size distribution may accelerate the rate of dissolution during droplet rise to the surface and therefore may have affected the concentrations of phototoxic PAHs at the surface. However, without an evaluation that can produce the concentrations of the phototoxic compounds that would result with or without dispersant use, the magnitude of the resulting changes in toxicity cannot be determined. For both these scenarios the resulting risk could be explored using coupled fate and effect models.

It should be noted that the tools to do such an evaluation are available. Models that predict the dissolved concentrations of various hydrocarbon blocks have been employed (see Chapter 2). The required toxicity models—PETROTOX and the phototoxic TLM—are also available. However, the effect of photo degradation of PAHs has not yet been included in the fate models. The PAHs that efficiently absorb incident light are also the PAHs that are susceptible to photo degradation. This is an important mechanism that also needs to be included in the fate models. The toxicity of the degradation products also needs to be included in the toxicity models.

A number of recent publications report phototoxic effects, including the effect of dispersants on photo toxicity (Alloy et al., 2017; Barron, 2017; Barron et al., 2018; Bridges et al., 2018; Finch and Stubblefield, 2016; Finch et al., 2016, 2017a,b, 2018; Nordborg et al., 2018; Overmans et al., 2018; Salvo et al., 2016). These tests cannot be evaluated to determine the effect of dispersants on phototoxicity of oil unless the concentrations of the dissolved components were measured at all the dilutions or unless the experiments were variable loading tests with measured total oil added (see Table 3.1). It is the same problem that limits the utility of the variable dilution toxicity tests. Additionally, only selective PAHs are phototoxic and their dissolved concentrations are required in order to confirm the cause of the observed toxicity.

Sediment Toxicity

Evaluating the toxicity of chemicals in sediments is complicated by the large variations in bioavailability to sediment-dwelling organisms due to variations in sediment composition. While not addressing oil contamination per se, in a classic paper by Adams et al. (1985) the observed LC50 (mortality) and EC50 (growth reduction) concentrations of the insecticide Kepone to the sediment-dwelling organism *Chironomus tentans* was < 1 μg/g for a sediment with low organic carbon concentration, $f_{OC} = 0.09\%$ by weight. By contrast, for a sediment with $f_{OC} = 1.5\%$ organic carbon, the EC50 and LC50 are approximately 7 and 10 μg/g, respectively. The high organic carbon sediment ($f_{OC} = 12\%$) exhibits still higher LC50 and EC50 values on a total sediment Kepone concentration basis, 35 and 37 μg/g, respectively (Adams et al., 1985). As a consequence, the dose metric employed for sediment toxicity tests must account for this.

The Kepone experiment provided two critical findings. The first was the observation that for these toxicity tests the pore water LC50 or EC50 varied only by approximately a factor of two for the three sediments, whereas the sediment LC50 or EC50 had an almost 40-fold range in Kepone concentrations. This pointed out the importance of the pore water concentration as a dose metric.

The second insight was the relationship of the pore water LC/EC50s and the LC/EC50s obtained from water-only exposures to the same organism. The pore water LC50s are 19 to 30 μg/L, and the water-only exposure LC50 is 26 μg/L. The pore water EC50s are 17 to 49 μg/L, and the water-only EC50 is 16 μg/L (Adams et al., 1985). This result suggested that if the concentration in the pore water equaled the LC50 or EC50 concentration for that organism in a conventional water-only exposure, the sediment would exhibit 50% mortality or 50% growth reduction. This observation suggested that the LC50s and EC50s obtained from conventional water-only exposures could be utilized to predict sediment toxicity.

The importance of pore water concentrations as a dose metric has prompted the development of methods to sample sediment pore waters directly (e.g., Arp et al., 2015). Until recently, however, methods for efficient and trustworthy sampling of sediment pore water were not available. The usual sediment sampling methods determined the chemical concentration in the total sediment. This included the chemical in the pore water and the chemical associated with the sediment particles and, if present, the chemical in condensed phases: for example, as a liquid or a solid. Two classes of models have been developed to evaluate the relationship between chemical concentrations in sediment and benthic organism toxicity (Wenning, 2005).

The first, referred to as empirical models, are based on large datasets of paired total chemical concentrations in the sediment and measured sediment toxicity. Various statistical methods have been employed to establish threshold and median concentrations for various chemicals (Long, 2006; Long et al., 1995, 1998).

The second, referred to as mechanistic models, deal with the bioavailability problem by utilizing models that predict the pore water concentration from the bulk sediment concentration and the relevant sediment properties (Di Toro et al., 1991). A comprehensive review and a comparison of the empirical and mechanistic models is available (Wenning, 2005).

Equilibrium Partitioning Model of Sediment Toxicity

The equilibrium partitioning (EqP) model was developed to establish sediment quality criteria (Di Toro et al., 1991). The EqP model assumes that the dose delivered from the pore water and the sediment solids exposure are equal if the pore water and sediment solids concentrations are in thermodynamic equilibrium. In this case, the chemical potential is equal in both phases and the compound in each phase exerts the same chemical binding strength toward the organism. Sediment criteria derived using the EqP model used the water-only aquatic life criteria concentration as the pore water concentration and predicted the bulk sediment concentration that would result for a sediment with a specific composition.

The TLM model was developed for the U.S. Environmental Protection Agency (EPA) sediment criteria development effort for PAH mixtures to predict the pore water concentrations for use in the EqP model (Burgess et al., 2012; Di Toro and McGrath, 2000; EPA, 2003). The model has been validated for individual PAHs in laboratory spiked sediments and also in PAH contaminated field collected sediments (Redman et al., 2014). It has been applied by EPA in the initial evaluation of sediment toxicity for the DWH oil spill (EPA, 2010, 2016a,b).

The application of the EqP-derived sediment toxicity concentrations requires a chronic exposure concentration. The reason is that sediment-dwelling organisms are exposed for either their partial or full life cycle. Therefore, the chronic criteria are appropriate. In the original EPA guidance documents (EPA, 2003), the chronic water quality criterion was employed. For application to this investigation, the chronic HC5 concentration can be employed. Figure 3.17 presents the chronic HC5 oil concentrations. Comparing Figure 3.17 (chronic HC5) to Figure 3.9 (acute HC5) illustrates the difference in concentrations for protection of acute exposures and mortality endpoints as well as chronic exposures and sublethal endpoints. The EPA sediment toxicity guidelines employ the latter.

Macondo Slick A and Slick B concentrations at TU = 1 can be used to provide the basis for a comparison to observed concentrations in the field, as shown next.

Comparison to Field Collected Data

Sediment Data

An example of TPAH concentrations in sediments is shown in Figure 3.18, for series of sediment cores collected during the DWH sampling cruises (Stout and Payne, 2016a).

The concentration units are mg TPAH/kg sediment, the concentration of TPAH per kg dry weight of sediment. An approximate comparison can be made using the TPAH concentration corresponding to chronic HC5 TUs = 1. The approximation employed is detailed in Di Toro and

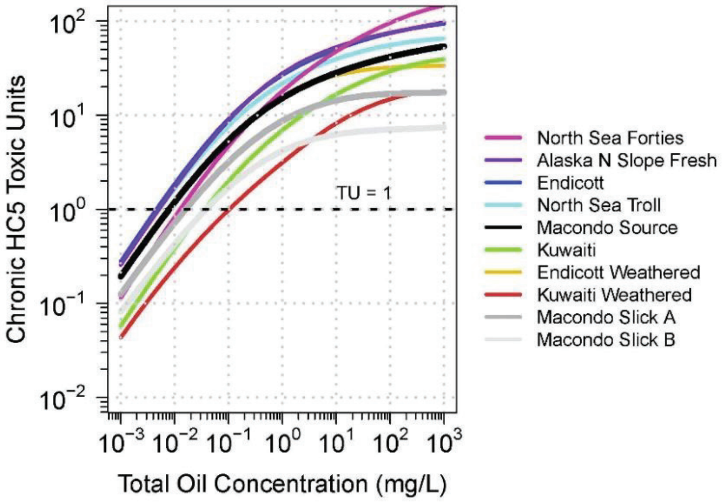

FIGURE 3.17 Chronic HC5 TUs versus oil concentrations (mg oil/L) for 10 oils. Dashed line at TU = 1. The chronic HC5 critical body burden required for the calculation is from McGrath et al., 2018.

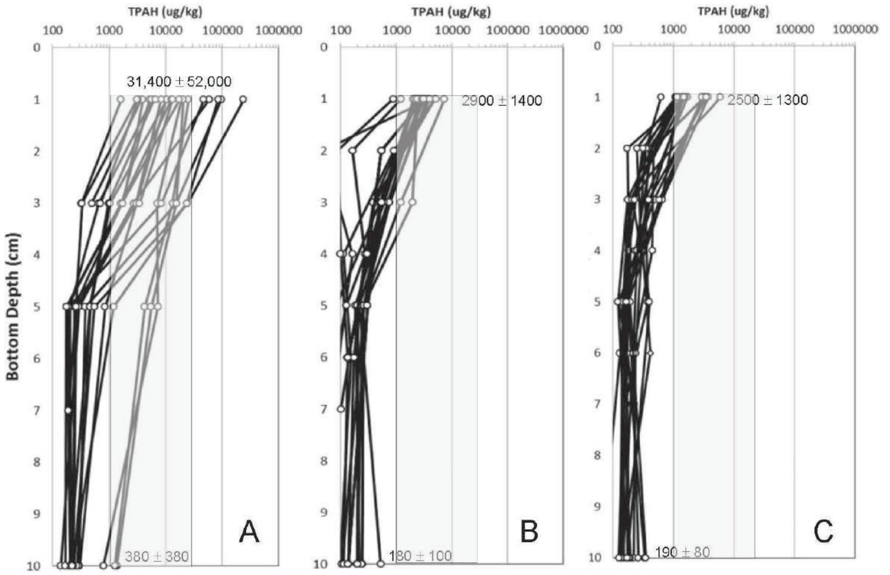

FIGURE 3.18 Comparison of chronic HC5 concentrations to observed TPAH concentrations. Caption reads: “Graphs showing the concentrations of TPAH50 in 2010/2011 cores containing wax-rich, severely weathered Macondo oil at the surface versus sediment depth for cores (A) 0 to 1.6 km (n = 23), (B) 1.6 to 4.8 km (n = 26), and (C) 4.8 to 8.0 km (n = 20) from the well. Bottom depths of each interval are plotted on y-axes.” Shaded region encompasses the chronic HC5 concentrations for the 5th to 95th fraction organic carbon (f_{OC}) percentiles from high-productivity areas (Seiter et al., 2004, Figure 2C). Concentrations in excess of the right-hand side of the shaded region exceed the chronic HC5 toxicity at the 95th percentile of f_{OC}. Concentrations less than the left-hand side of the shaded region are lower than the chronic HC5 toxicity at the 5th percentile of f_{OC} and would not exceed the chronic HC5. The toxicity of the concentrations in the shaded region cannot be determined without the fraction organic carbon of that sediment sample. SOURCE: Modified from Stout and Payne, 2016a.

McGrath (2000). The required sediment concentration is the organic carbon normalized concentration (mg TPAH/kg sediment organic carbon.) In order to make the comparison, the fraction organic carbon in the sediment is required. The shaded box in Figure 3.18 enclose the TPAH sediment concentrations (mg TPAH/kg sediment) that are within the fraction organic carbon spanning the 5th and 95th concentrations (0.00208 and 0.0428 gOC/g sediment) found in sediments from productive regions areas (Seiter et al., 2004, Figure 2C). As a comparison, the Long and Morgan effects range low (ERL) empirical sediment criteria for the sum of TPAHs (Long et al., 1995) are quite close to the TPAH chronic HC5 concentration. For $f_{OC} = 0.01$ gOC/g sediment, the ERL = 4.64 and the chronic HC5 = 5.32 mg TPAH /kg sediment. Most of the sediment concentrations within 1.6 km of the discharge and the surface samples at all distances sampled are in the uncertain range. It is not possible to make the comparison to the chronic HC5 for these data. This comparison highlights the importance of expressing sediment concentration as organic carbon normalized concentrations (EPA, 2003). For a more complete analysis, the following also need to be considered: the TPH that are present in addition to the TPAH; other sediment phases that sorb PAHs such as black carbon (Ghosh, 2007; Lohmann et al., 2005), and the extent that the sorption is reversible (e.g., Fu, 1994).

Water Column Data

A selection of water column field data is presented in Figure 3.19 (Boehm et al., 2016). The concentration units are mg TPAH/L. A conversion of these concentrations to TUs is necessary for the same reason that it is required for the sediment data. The conversion requires the individual PAH concentrations and an estimate of the concentration of microdroplets in order to obtain the dissolved PAH concentrations. The necessary acute and chronic HC5 concentrations are available for the calculation of the TU concentration (see Figures 3.9 and 3.17, respectively). The choice for using the acute HC5 for the water column and the chronic HC5 for sediments is made because there are no duration-specific criteria and this choice is conventional. As pointed out above, the effect of exposure time is substantial.

The acute and chronic HC5 concentrations for MASS oil are approximately 1,000 and 10 mg oil/L. These correspond to approximately dissolved TPAH concentrations of 10 and 0.5 mg TPAH/L

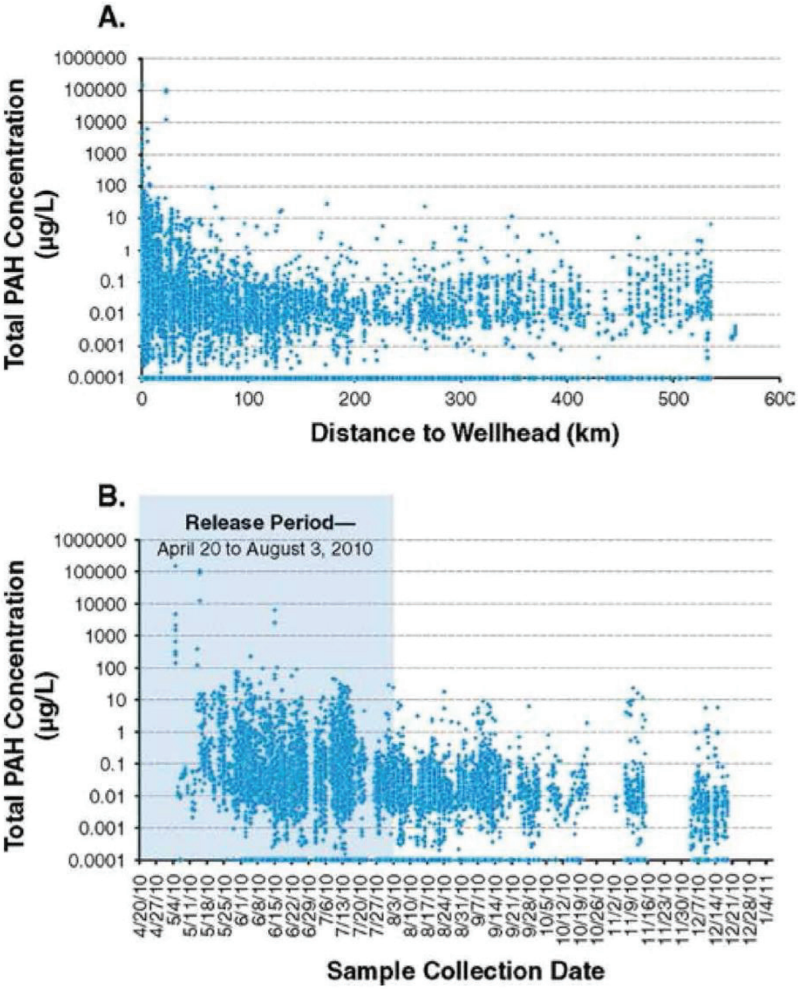

FIGURE 3.19 Compilation of DWH water column TPAH concentrations. Figure caption reads: "Total polycyclic aromatic hydrocarbon (TPAH) concentrations of all water samples as a function of distance (A) and time (B). Samples with nondetectable TPAH were set to 0.0001 ppb for plotting on a log-scale graph." SOURCE: Boehm et al., 2016.

(see Figure 3.11A). During the release period (see Figure 3.19B), most of the observed TPAH concentrations are below the acute HC5 (10 mg TPAH/L), and they bracket the dissolved chronic HC5 (0.5 mg TPAH/L). Because the TPAH concentrations in the field data include the microdroplet contribution, which could be significant (see Figure 3.11A), it would need to be subtracted from the observed concentrations in the field in order to judge the extent of toxicity. This illustrates the need to make the appropriate measurements of dissolved oil components so that a direct estimate of TU concentration can be made.

The above analyses are presented in order to highlight the problems that are encountered if a direct comparison of field TPAH concentrations and acute and chronic HC5 TPAH are compared. The field data from the DWH could be used to calibrate and validate exposure predictions using fate models that incorporate both surface and subsurface dispersant at the rates and timing applied during the response. Such exercises are necessary in order to understand quantitatively the effect that the use of dispersants could have on water column and sediment toxicity. In the case of the DHW, the use of dispersants potentially increased the mass of oil reaching the sediments through the formation of oiled marine snow (see Chapter 2). Therefore, a reevaluation and reinterpretation of the field data from the DWH are required in order to understand the magnitude and extent of toxicity.

Evaluating the effect that the use of dispersants had on the resulting water column and sediment toxicity can only be made using models that compute the changes in fate and the resulting toxicity with and without dispersant addition. For example, the presence of dispersants potentially increased the mass of oil reaching the sediments through the formation of oiled marine snow (see Chapter 2), which increases the rate of deposition to sediments with the combination of oil, dispersants, and clay minerals forming oil-mineral aggregates. In the case of the DWH and Ixtoc I blowouts, the addition of large quantities of dispersants apparently increased the intensity of oiled marine snow, resulting in elevated toxicity to benthic organisms (Daly et al., 2016; Vonk et al., 2015).

A PATH FORWARD FOR AQUATIC TOXICITY TESTING

Test Standardization

As discussed in the sections above, the specific parameters used to prepare WAF or CEWAF (i.e., mixing energy, preparation method) have an effect on the composition of hydrocarbons in the exposure media, thus influencing their toxicity. Consequently, the comparability and reproducibility of toxicity data, as well as their practical application to spill situations, require the consistent use of standardized test procedures. While this is not a novel concept (e.g., CROSERF; Aurand and Coelho, 2005; NRC, 2005), the lack of adherence to existing toxicity testing methods continues to be an issue. As a result, recent efforts have further advocated for standardization of test procedures (Bejarano et al., 2014b; Coelho et al., 2013; Hodson et al., 2019; Redman and Parkerton, 2015). The test procedures originally proposed by CROSERF sought to provide a consistent framework for generating and interpreting toxicity test results. Although the initial framework proved to be comprehensive, modifications were proposed more than a decade ago in the previous NRC report (2005), and NRDA researchers have since suggested more modifications (Forth et al., 2017a; Krasnec et al., 2016).

This current evaluation of the toxicological effects has again emphasized the need to update the CROSERF protocols based on an increased understanding of exposure and uptake and to align with current state-of-the-art technology for solution preparation and analysis. Examples of proposed updates include:

- Conduct (and report) detailed chemical characterization of the source oil that is used in the toxicity test.
- Examine the relevance of mixing energy of WAFs to generate useful data that can be used to validate toxicity models, and also identify a single mixing energy that can be used to prepare WAFs and CEWAFs (to allow for dataset comparison).
- Eliminate the use of HEWAF preparations that generate excessive microdroplets unless there is conclusive evidence to justify that these high concentrations occur in the real world.
- Standardize toxicity test dispersant-to-oil ratios for CEWAFs to align with operational use (e.g., 1:20 for surface dispersant application and 1:100 for SSDI).
- Expand research to include all dispersants likely to be employed in the global dispersant stockpile (not just Corexit®).
- Reserve declining concentration exposure regimes such as spiked exposures for specific situations when appropriate because the chemical exposure from most spills is constantly changing and is exceedingly difficult to quantify. Instead, consider a few constant exposure periods that could equate to short exposures resulting from using dispersants on a batch spill (few hours) to longer exposures that could equate to arctic, cold weather, or prolonged subsea exposure.
- Expand chemical characterization to include as many individual constituents as possible (> 50+ PAHs), including all the hydrocarbons, based on latest analytical capabilities.
- Analyze unfiltered and filtered water samples or passive sampling of the dissolved concentration of each test solution to account for relative contribution of microdroplets.
- If the variable loading method is adopted, develop and standardize analytical protocols that focus on dissolved oil exposures (e.g., filtering or passive sampling).

One potential mechanism to make these modifications to CROSERF is to create a working group of toxicologists, modelers, and resource trustees to ensure that these modifications will support future needs for science to support the operational response community. Future modifications should emphasize the need to generate toxicity data that will inform, validate, or improve toxicity models. Ultimately, having better toxicity models will help response decision makers and response personnel make informed decisions about dispersant use based on the best available information.

Passive Dosing and Passive Samplers

More sophisticated systems have emerged in recent years to generate toxicity data using continuous exposures in a flow-through system (Nordtug et al., 2011). This system enables the quantification of the relative contribution of both dissolved oil fractions and oil droplets to the overall short- or long-term toxicity to aquatic species. For example, this flow-through test system was used to assess the toxicity of physically and chemically dispersed oil to cod larvae (Hansen et al., 2019). This study provided additional evidence on the limitations of total PAH as an exposure metric in oil toxicity, further demonstrating the limited role that oil droplets play in driving toxicity. These systems are also promising as they may provide the necessary link between laboratory and field measurements and observations.

An alternate approach for preparing exposure media and understanding the toxicity of WAF and CEWAF is the use of passive dosing techniques. In recent years, passive dosing approaches have been developed to generate and maintain stable aqueous concentrations of hydrophobic chemicals, including hydrocarbons. Passive dosing commonly employs silicone polydimethylsiloxane (PDMS) tubes. PDMS tubes are loaded with a test solution and directly immersed in water allowing the continuous partitioning of freely dissolved material through the permeable membrane into the aqueous exposure media. This approach alleviates the interference introduced in toxicity data by oil microdroplets while controlling for compound losses due to volatilization. When placed in test systems, PDMS tubes loaded with known oil concentrations (i.e., WAF or CEWAF) serve as a passive dosing source of dissolved oil in toxicity tests. Such experiments have been successfully carried out with single hydrocarbon compounds, hydrocarbon mixtures, and crude oils under acute and chronic exposures (Butler et al., 2013, 2016; Letinski et al., 2014; Redman et al., 2018; Renegar et al., 2017a). Furthermore, one study demonstrated that passive dosing produces comparable exposures of dissolved oil as WAF generated with the CROSEF method (Bera et al., 2018).

Similarly, the use of solid-phase microextraction (SPME) polymer fibers as passive samplers have also been proposed as cost-effective tools in the quantification of freely dissolved chemicals (Leslie et al., 2002; Mayer et al., 2014; Verbruggen et al., 2000). Because SPMEs serve as a surrogate hydrophobic phase of lipids, dissolved constituents in an aqueous exposure media would partition to SPMEs simulating bioconcentration and providing a quantifiable dose metric. Analytical chemical characterization of SPMEs could then be interpreted to represent bioavailable dissolved concentrations. SPMEs coated with PDMS have been tested and used with hydrocarbon mixtures and crude oils (Letinski et al., 2014; Parkerton et al., 2000; Redman et al., 2018), but their use in toxicity testing carries nuances (i.e., equilibrium with the exposure media and negligible depletion of dissolved-phase concentrations) that need to be carefully considered (Redman and Parkerton, 2015). While the use of passive dosing and sampling approaches is promising, further standardization of test procedures is needed to ensure their inter-laboratory comparability and reproducibility.

While understanding the consequences of oil spills (with or without dispersant use) on exposed populations is of high importance, these cannot be made solely based on results from laboratory studies. Such assessments involve the integration of complex biological and ecological knowledge, including effect responses (e.g., laboratory and field exposures) at different levels of biological organization, life-history parameters and population structure, environmental drivers of population dynamics, etc. Related efforts have been undertaken (e.g., Fodrie et al., 2014; Gallaway et al., 2017), suggesting that effect responses (sublethal or lethal) on individuals may not necessarily translate into population-level impacts. These and related studies point to the need for better integrating aquatic toxicology studies with knowledge on other factors that determine population viability.

BIOLOGICAL EFFECTS

The exposure of aquatic species to the toxic fractions in oil under field conditions depends on the rate at which petroleum hydrocarbons partition and dilute into the water column, with a greater petroleum hydrocarbon exposure potentially resulting from the use of chemical dispersants, although the combination of dilution, dispersion, and biodegradation serves to reduce aqueous concentrations significantly and rapidly. Slow moving or immobile aquatic species and life stages that are entrained within water masses containing physically and/or chemically dispersed oil may be at greater risk of exposure to dissolved oil fractions. Even when entrained within a water mass, physical processes and water column mixing dilute dissolved oil fractions, making exposures variable over time. As a result, one of the greatest limitations in understanding the potential impacts related to dispersant use in open waters is the lack of data derived from exposure conditions that capture the environmental realism of most oil spills (Aurand and Coelho, 2005; Bejarano et al., 2014b; Clark et al., 2001). Even greater uncertainties and data limitations exist when understanding potential impacts from subsea dispersant injection. This is due in part to the difficulty of working with deepwater species as they require special conditions, including high pressure, low temperatures, and darkness.

Despite these limitations, toxicity data from controlled laboratory studies provide conservative estimates of potential impacts. Exposure of aquatic species—particularly early life stages—to physically and chemically dispersed oil can lead to lethal and ecologically important sublethal impacts, but the onset of these impacts depends on several factors, among them concentrations of dissolved hydrocarbon fractions, exposure duration, and species/life stage sensitivity to oil. A growing body of literature (e.g., Carls et al., 1999; Esbaugh et al., 2016; Heintz et al., 1999; Incardona et al., 2004, 2011, 2013; Mager et al., 2014) has shown that under controlled laboratory conditions, fish embryos exposed for several hours post hatch to low PAH concentration (in the low μg/L) may develop gross abnormalities, with permanent impacts potentially causing reduced survival later in life (Incardona et al., 2013).

In their recent review *The Toxicity to Fish Embryos of PAH in Crude and Refined Oils*, Hodson et al. (2017) present a series of conclusions that can be analyzed and compared using the TLM.

- "3-5-ringed nonsubstituted, alkylated, hydroxylated, and heterocyclic PAH[s] cause effects on fish embryos that closely resemble those of crude and refined oils;
- Alkyl PAH[s] are the predominant congeners in crude and refined oils. Their toxicities must be considered in assessments of the ecological risks and impacts of oil spills;
- The embryo toxicity of PAH[s] increases predictably with an increasing [of] the number of rings, alkyl carbons, and Kow, indicating that water–lipid partitioning controls exposure and tissue dose; . . . ."

The TLM toxicity prediction is the sum of the TUs of all the components of oils, in particular alkylated, hydroxylated, and heterocyclic PAHs. Predicted toxicity increases as K_{OW} increases.

- "There are significant differences in embryotoxicity among PAH, which can be associated with the pattern of alkyl substitution, but not with Kow; . . . ."

This level of molecular detail is not part of the original TLM. It could be investigated using the more recent TLM model that uses additional molecular properties (e.g., molecular polarizability, dipole-dipole and dipole-induced dipole interaction, and hydrogen bonding) to predict the toxicity from molecular structure (Boone and Di Toro, 2019; Kipka and Di Toro, 2009).

- "Chronic EC50s for individual PAH[s] range from 0.3 to 100 [μg/L]."

A recent reevaluation of the TLM that expands the chronic toxicity database results in chronic HC5s ranges that are quite close: from approximately 0.085 μg/L to 200 μg/L for PAHs with $\log K_{OW} = 6.5$ to 2.5 (McGrath et al., 2018).

- "Because crude oil includes some PAH[s] that induce CYP1A enzymes, all PAH[s] in oil will be subject to higher rates of oxygenation, even if they are not inducers;
- The potentiation and antagonism of CYP1A metabolism and toxicity of PAH[s] in mixtures suggest that measured toxicities of single PAH[s] are conservative and may not be a sound basis for predicting the impacts of mixed PAH[s] from an oil spill; . . . ."

This is a molecular level interaction that can be addressed with the modern models that use molecular properties to assess toxicity as discussed above.

- "Because mixture interactions are not well studied, TPAH concentrations 0.1 μg/L following oil spills should be considered hazardous."

The use of TPAH concentrations as the dose metric is not consistent with the large variation in toxicity of the individual PAHs. The only currently available experimentally validated mixture model is TUs. If a more reliable mixture model is developed and validated, then it can be used.

When reviewing these laboratory studies, the reader is cautioned to carefully consider how the exposure media were prepared (especially with respect to presence of microdroplets) as well as how the chemistry was conducted and reported. Also, the environmental relevance of these species and life stages, in the context of the specific marine ecosystem, merits consideration. One of the reasons that dispersant application is generally not considered close to shore is to prevent the introduction of dispersed oil into shallow and/or nearshore environments (e.g., in the vicinity of many fish nursery habitats). Dispersant use in marine offshore environments involves trade-off decisions (see Chapter 6), with the recognition that early life stages (generally assumed to be more sensitive to oil) and entrained species may be at increased risk of exposure.

As a point of reference, 75% of water samples collected during the DWH oil spill had TPAH concentrations (sum of 50 parent and alkylated PAHs) of < 1 µg/L, though water samples in the vicinity of the wellhead had concentrations $> 1{,}000$ µg/L (Boehm et al., 2016; see Figure 3.19). Concentrations in excess of 1 µg TPAH/L were generally within 20 km of the wellhead at depths of 1,000-1,200 m and in the top 3 m of the water column under surface oil (Boehm et al., 2016). Field assessments of dispersant effectiveness found average TPAH concentrations in the top 1 m of the water column of 10.5 µg/L following "very effective" surface dispersant applications, which rapidly and substantially diluted in less than an hour (Bejarano et al., 2013). This type of rapid dilution is frequently overlooked in laboratory studies.

Many studies have been conducted that examine the sensitivity of cold water species to dispersed oil. Most of these studies have used crude oil or individual polycyclic aromatic compounds and have exposed copepods and fish larvae (e.g., Baussant et al., 2009; Christiansen et al., 1996; Grenvald et al., 2013; Hansen et al., 2011; Hjorth and Nielsen, 2011; Ingebritsen et al., 2000; Jensen and Carroll, 2010; Jensen et al., 2008; Perkins et al., 2005; Skadsheim et al., 2009). Studies looking at both physically and chemically dispersed oil have demonstrated that the toxicities are essentially the same provided that field relevant concentrations are used (e.g., Gardiner et al., 2013; Hansen et al., 2012; McFarlin et al., 2011). These studies further showed that while dispersants temporarily increase the bioavailability of oil, the acute toxicity from the dispersants resulted only at much higher concentrations than would be expected in the water column following an appropriate application of dispersant.

It can be challenging to obtain regionally specific toxicity data because of practical limitations associated with testing Arctic species in standard laboratory test. Therefore, several studies have considered the possible applicability of temperate species toxicity data to Arctic species (Bejarano et al., 2017; de Hoop et al., 2011; Gardiner et al., 2013; Olsen et al., 2016). Studies suggest that cold water species have similar sensitivity as do temperate species to petroleum-related compounds based on acute effects. The Norwegian Research Council reached a similar conclusion based on reviews of research conducted over a 10-year period on the long-term impacts of the oil and gas sector on the environment (Norwegian Research Council, 2012). According to multiple studies, however, cold water species may take longer to exhibit effects from hydrocarbon exposures (Chapman and Riddle, 2005; Gardiner et al., 2013; Hansen et al., 2013; Olsen et al., 2011). Increased response time of cold water species may be attributed to morphological and physiological adaptations for cold water survival that may impact toxic responses, such as increased lipid stores and decreased metabolism (de Hoop et al., 2011). Although similar comparative studies are still needed for deepwater species, limited empirical data suggest that their sensitivity is also comparable and within the range of sensitivity of temperate and shallow-water species (e.g., Frometa et al., 2017; Knap et al., 2017; McConville et al., 2018).

In addition to liquid oil released at depth, gas also escapes. The high pressure at depth increases the solubility and therefore the exposure of organisms to low molecular weight dissolved hydrocarbons (e.g., methane, ethane, etc.). However, the increased pressure also decreases the toxicity of these compounds. The required toxicity pressure corrections have been developed for use in the TLM (Paquin et al., 2018).

Apart from the direct impacts of oil and dispersed oil on mortality of various species and life stages, there are a wide variety of sublethal effects (e.g., physiological, immune, structural, and behavioral responses) that can lead to negative outcomes. These include alterations of vital rates (e.g., growth, fecundity), compromised immune functions, and other stressors, leading, in some cases, to susceptibility to other pathologies. Oil spill effects on growth rates of larvae (e.g., Hernandez et al., 2016) and adult fishes (e.g., Herdter et al., 2017) have been well documented in the literature. What is unclear is the role that dispersed oil plays in these changes.

Despite the relatively low oil concentrations observed in field-based assessments of DWH, particularly at some distance from the wellhead, recent research has also emphasized that even very low concentrations (single digits to < 1 μg/L) of oil exposure can have severe sublethal impacts resulting in impairment of cardiac function (Brette et al., 2014; Incardona et al., 2014); larval developmental anomalies; reduced physiological performance; compromised sensory systems and behavior; impacts on microbiomes; altered immune function; DNA damage and oxidative stress; compromised reproduction; and other serious effects (see Grosell et al., in press, for a review of recent literature). These symptoms can be significant for the individual, but if a sufficient fraction of the extant population is exposed, it can result in lower overall fitness, in reductions in recruitment (survival of young), and in reduced population viability. This may be particularly important with respect to long-lived animals, those already reduced because of other factors, or populations with limited geographic ranges.

Few studies have evaluated such factors based on laboratory control of exposures, although some studies exist. These vital rates are important to populations because the overall fitness of an animal population is determined by the number of viable offspring it produced. In the case of fishes, fecundity is both a logarithmic function of size (length) and a linear function of body weight. Thus, if growth rates of adults are suppressed, this will lead directly to lower overall egg production. Furthermore, if those larvae produced have poor condition and survival, this too will result in lower production and thus lower fitness of the population. Studies showing sublethal impacts, including cardiac dysfunction (Incardona et al., 2014), behavioral impairment (Stieglitz et al., 2016), and other negative physiological effects (Whitehead et al., 2011), can lead to mortality (especially for larvae). They may also lead to impaired population fitness. It is thus important to consider sublethal impacts, including those directly related to population vital rates, when considering the effects of toxic exposures from the population life cycle perspective.

For more than 20 years, there has been concern that if oil spills (and other toxic substances) result in genetic mutations, these could be passed along through subsequent generations, resulting in decreased fitness of populations in perpetuity (Cronin and Bickham, 1998). Surprisingly, little research on the heritability of mutations due to oil exposure has been conducted following the study of White et al. (1999). Several studies have, however, identified genomic and transcriptomic changes in various organisms (e.g., Whitehead et al., 2011; Xu et al., 2016), including fishes, although the phenotypic consequences of genomic modifications resulting from oil exposure have not been obvious in many cases. This merits priority for future research because of the potential long-term consequences for populations and ecosystems.

Sensitive Habitats

In recent years, literature reviews have been published on the impacts of oil spills on shoreline or nearshore habitats (Bejarano and Michel, 2016; Duke, 2016; Michel and Rutherford, 2014; Turner and Renegar, 2017). In general, the scale of impacts and speed of recovery varies depending on the spill size and the magnitude of response actions or treatment intensity. However, because of their specific focus, some of these reviews have included only limited discussions related to dispersants. While spills of opportunity have provided valuable information on the impacts of oil on sensitive habitats, most have not involved the use of dispersants. Thus, the lack of comparative field studies on the impacts of treated versus untreated oil has restricted the understanding of the hazard posed by dispersant use. One exception has been the 1984 Tropical Oil Pollution Investigations in Coastal Systems (TROPICS) field study (reviewed in NRC, 2005). The TROPICS is the longest monitored field study. It has been monitored for 25-plus years to assess the impacts of chemically dispersed oil on nearshore shallow-water (< 1 m depth) habitats (Ballou et al., 1989). This field study simulated maximum exposure from a single dispersant application for exposures of intertidal mangroves, subtidal seagrass, and shallow-water corals to Prudhoe Bay oil released in boom-enclosed areas (900 m^2) and chemically dispersed with Corexit® 9527. Monitoring within 2 years post exposure found declines in the abundance of corals and associated fauna as well as reduced coral growth rate in one species in the chemically dispersed area (Ballou et al., 1989), with complete recovery after 10 years (DeMicco et al., 2011). In contrast, oil penetrated the substrate at the non-dispersed site, serving as a source of hydrocarbons to adjacent habitats (DeMicco et al., 2011). As a direct result of hydrocarbon leaching from the substrate, seagrass beds of *Thalassia testudinum* at the non-dispersed area had a 58% decrease in coverage and slower growth rates compared to the chemically dispersed area (Baca and Getter, 1984; DeMicco et al., 2011). Other field studies have also documented higher oil persistence in nearshore sediments of untreated oil areas compared to areas treated with dispersants (reviewed in NRC, 1989, 2005; see also Blackall and Sergy, 1981; Gilfillan et al., 1986, for details). For example, the 3-year investigation of the Baffin Island Oil Spill Project showed lower incorporation of petroleum hydrocarbons in Arctic subtidal sediments following an experimental release near the bottom of chemically dispersed (Corexit® 9527) Lagomedio crude oil than did a release of untreated oil (Boehm et al., 1987).

Although field studies in nearshore areas have provided valuable information, it is important to note that at least in the United States, dispersants are not preauthorized for use in shallow waters (generally < 10 m depth, or < 3 nautical miles from the shoreline), and that best management practices are in place to minimize impacts of response actions on sensitive habitats. Deepwater benthos in offshore marine environments may be exposed to oil by the transport of organic and inorganic particles from the upper layers of the water column via particle formation and sinking through a number of processes (see Chapter 2). However, the role of particles in transferring oil to deeper waters with and without the use of dispersants is not well understood.

Wildlife

Surface or subsurface dispersant use results in small oil droplets with larger surface-to-volume ratios that enhance the dissolution of soluble and semi-volatile compounds, resulting in lower concentrations of airborne volatiles and enhancing safety for response workers (Curd, 2011; Gros et al., 2017; see Chapters 2, 4, and 7 for details). This also potentially reduces impacts to air breathing wildlife at the water surface. Despite this potential reduction in exposure to volatile compounds, the hazard posed by dispersant use to wildlife under field conditions is not fully understood because it is difficult to differentiate the impacts of chemically dispersed oil from those of physically dispersed oil. Most of the current knowledge on oil spill impacts to wildlife has been generated through controlled laboratory exposures or from real-world incidents that did not involve the use of dispersants.

It is generally well known that cetaceans could be susceptible to the inhalation of volatile oil fractions and to the inhalation and aspiration of oil droplets at the water surface, which could cause tissue damage along the respiratory tract and lungs, resulting in inflammation of airways, lung disease, and pneumonia (Engelhardt, 1983; Geraci and Aubin, 1988; Schwacke et al., 2013; Takeshita et al., 2017). Inhaled or aspired oil could result in prolonged exposures to lung tissue or in the absorption of hydrocarbons into the bloodstream during long dives. There is evidence from laboratory studies that dispersant use to treat oil slicks causes aerolization of small oil droplets (Afshar-Mohajer et al., 2018) at the water surface-air interface where cetaceans breathe. Although these droplets could be aspired into the blowhole of cetaceans, the degree of exposure and the implications on their health are not fully understood and require further investigation. While this exposure pathway is a source of concern, best management practices are in place during surface dispersant applications to minimize direct exposure to marine mammals, which would reduce the likelihood of exposure to aerosolized oil droplets. These practices include having trained wildlife observers confirming the absence of cetaceans, birds, and turtles within 1 km of aerial dispersant operations.

Compared to cetaceans, oils spills pose a greater fouling hazard to furred marine mammals, marine sea turtles, waterfowl, and diving birds, because they spend large amounts of time at the water surface. Thus, effective chemical dispersion of surface slicks may decrease oil concentration and thickness, potentially reducing the risk of exposure to these wildlife. Sea turtles could be exposed to oil at the water surface via inhalation of volatile fractions and ingestion of oil mistaken as food, which could cause skin irritation and lesions as well as alteration of respiration and diving patterns (Albers and Loughlin, 2003; Curd, 2011; Lutcavage et al., 1995; Lutz and Lutcavage, 1989; NRC, 2013). For example, following the Ixtoc I and DWH oil spills, large numbers of sea turtles were found to have oil in their oral and nasal cavities and in their digestive tracts (Hall et al., 1983; Mitchelmore et al., 2017). A study on the impacts of chemically dispersed oil on sea turtle embryos resulted in no adverse impacts (Van Meter et al., 2006). Commonly reported impacts of oil spills on birds are associated with dermal exposure and fouling, which reduces buoyancy, water repellency, and insulation provided by feathers and leads to disruptions in thermoregulation, causing hypothermia (Duerr et al., 2011; Jenssen, 1994; Jenssen and Ekker, 1991; NRC, 2005; O'Hara and Morandin, 2010; Whitmer et al., 2017). Laboratory studies have found that chemically dispersed oil alters the structure and geometry of common murre (*Uria aalge*) feathers, causing a disruption of waterproofing properties (Duerr et al., 2011). A related study also found that both physically and chemically dispersed oil reduced waterproofing of this same species in a dose-dependent manner (Whitmer et al., 2017). Although the same study found negative impacts on waterproofing following direct exposure to Corexit® 9500A alone, best management practices are in place during surface dispersant applications to minimize direct dispersant spraying of wildlife. Direct application of undiluted Corexit® 9500 to mallard (*Anas platyrhyncos*) eggs also led to embryotoxicity (i.e., reduced hatching success, altered development) (Wooten et al., 2012), though this direct exposure pathway is unlikely as dispersants are not intentionally applied to adult birds or developing eggs.

Given the relatively limited information, it is clear that studies are needed to address the uncertainties associated with the impacts of chemically dispersed oil relative to floating oil and physically dispersed oil on wildlife. Although a similar conclusion was reached by NRC previously (NRC, 1989, 2005), relatively few studies have been conducted since those recommendations were made. The current state of science is to use oil thickness as the dose metric. See French-McCay (2016) for a review of studies used to establish screening thresholds for oil thickness to wildlife and shore habitats. It is unclear, however, whether this is the correct dose metric, whether the suggested thresholds are correct, and whether the same threshold applies for chemically and physically dispersed oil. In addition, other exposure pathways (e.g., inhalation of vapors or oil aerosols, ingestion of contaminated diet) are not considered.

APPLICATION TO THE CONTEXT OF FIELD EXPOSURES

When considering dispersant use for a spill response scenario, it is important to acknowledge the hazards to aquatic resources due to the toxicity of the oil itself. Unmitigated floating oil slicks pose significant hazards to wildlife, especially animals that rely on the surface of the ocean to rest, feed, or breathe air. During higher sea states, untreated oil will be naturally dispersed, resulting in elevated hydrocarbon concentrations even without the use of dispersants. So, the decision to use dispersants must account for the risks posed by untreated oil as compared to the risk of chemically dispersing the oil (see Chapter 6). One important consideration is the extent and speed of habitat and population recovery after initial impact. Another important consideration is the broad range of sensitivity among species—and life stage sensitivity differences within a single species—so proper identification of the species (and life stages) present in any area where dispersant use is being considered is needed to make sound decisions (see Chapter 6).

It is also important to recognize that ongoing scientific research plays an important role in increasing our understanding of environmental challenges in the context of potential dispersant use. Because each spill has its own challenges and environmental settings, the practical application of scientific knowledge, especially from toxicity studies, may not be direct because most of the available data may not represent typical environmental field conditions. Disparities arise from the fact that the hypotheses being tested by scientists in the laboratory may not always align with the scientific needs of spill responders in the field. Generally, exposure concentrations under laboratory conditions are held relatively constant for a prolonged period to ensure that dosing is sufficiently high to elicit a toxicological response. In contrast, more representative test protocols for operational decisions are those from exposures that allow for water mixing and dilution during the exposure period (e.g., Aurand and Coelho, 2005; Bejarano et al., 2014b; Clark et al., 2001). As a result, what is toxic under controlled laboratory conditions, even those from more representative, declining exposures, does not necessarily translate into similar effects under field conditions.

New scientific information has been generated through the NRDA process from multiple prior oil spills. To support injury assessments and damage quantification, NRDA generates information using reproducible standard scientific approaches, which often involve toxicity testing under controlled laboratory conditions. However, some of the same constraints previously described may also apply to data developed under the NRDA protocols. Despite these challenges, scientific knowledge from laboratory exposures is valuable because such knowledge answers important questions on how aquatic organisms respond to oil exposures. Furthermore, laboratory toxicity studies have facilitated the development of models that provide a scientific link between laboratory and field exposures and effects.

The development of the models described in this chapter relies on the toxicity data generated from toxicity tests. Rather than developing toxicity tests that attempt to simulate the exposure and duration in field exposures, the committee recommends that toxicity tests be designed to calibrate and validate the toxicity models at environmentally realistic concentrations. The toxicity models would be used together with environmental fate models discussed in Chapters 6 and 7 to evaluate the exposure and toxicity associated with various response options, in particular, the potential costs and benefits of dispersant use.

In order to evaluate the impact of dispersant use, it is important to understand the complexity of exposures that generally occur under field conditions. In the water column, the toxicity of physically or chemically dispersed oil relates to these four factors:

1. Concentration exceeding known acute or chronic toxicity thresholds for the specific oil;
2. Duration of exposure above toxic thresholds;
3. Spatial and temporal distribution of marine life; and
4. Species sensitivity to oil exposure above the acute or chronic toxicity thresholds.

When examining the expected initial concentrations of dispersed oil, it is important that both lethal and sublethal (e.g., impairment in growth, reproduction, respiration rates) effects are considered. Laboratory tests can identify species thresholds both for mortality and for these other serious sublethal effects. Figures 3.9 and 3.17 present examples of acute and chronic HC5 concentration, which accounts for species sensitivity by setting the effect concentration that is protective of 95% of the tested species using the SSD.

The use of these laboratory results to assess the potential risks of dispersed oil to marine life provides an incomplete understanding of the potential effects in the ocean, because laboratory data rarely approximate field exposure. Open ocean field experiments conducted in the North Sea showed rapid dilution of dispersed oil concentrations following dispersant application (see Box 6.1). The rapid dilution of dispersed oil is also documented in a literature review (Bejarano et al., 2014b) that included field measurements from extensive studies during the DWH spill (OSAT, 2010), in which less than 1% of water samples analyzed exceeded aquatic toxicity benchmarks. Furthermore, many mobile marine organisms may display an avoidance behavior, not remaining in a region with continual exposure to dispersed oil. As a result of the different exposure durations, a direct comparison between laboratory and field effects is problematic (Aurand and Coelho, 2005; Bejarano et al., 2014b; Clark et al., 2001; IPIECA, 2015). For these reasons, it is logical to calibrate a coupled exposure and effects model under laboratory exposure conditions using a given oil to predict toxicity under different exposure conditions for other oils.

Despite the limitations of extrapolating laboratory to field effects, efforts have been made to find practical applications of the substantial toxicity data produced over several decades. The Coastal Response Research Center sponsored a project in 2013 to make toxicity data for dispersants, oil, and dispersed oil more readily available by centralizing toxicity data. The end result is a data compilation that provides a quantitative basis for a more thorough assessment of hazard concentrations (Bejarano et al., 2016; NOAA ERD, 2015). This new tool has been incorporated into the NOAA Chemical Aquatic Fate and Effects database, allowing users to quickly develop SSDs to improve hazard estimates during oil spill response activities and exercises. The database enables users to filter information that specifically relates to a particular oil or dispersant, which allows decision makers to rapidly access past research and apply it in a meaningful way. From a practical perspective, the use of SSDs is advantageous because:

- SSDs provide potentially useful information to stakeholders involved in oil spill response decision making.
- Even when the SSDs are based on standard laboratory exposures rather than real-world exposure regimes, they can provide scientifically defensible benchmarks for dispersant use decisions.
- In the absence of toxicity data for species in extreme environments—such as Arctic and deepwater—adjustments to the SSD can be made to predict the change that might result to the HC5.

Finally, in recent years there has been dramatic expansion of toxicity research well beyond the organismal unit into areas of metabolomics, genetics, species interactions, and ecosystem-level responses (*Deepwater Horizon* Natural Resource Damage Assessment Trustees, 2016; Tarnecki and Patterson, 2015). More recent studies are also advancing the understanding of the effects of oil and dispersed oil exposure when compounded by other environmental stressors, such as UV radiation, temperature, salinity, etc. While these advances in science offer new insights into oil toxicology, the scientific community should remain vigilant about appropriate interpretation of these data and meaningfully communicating appropriate results to the operational response community.

FINDINGS AND RECOMMENDATIONS

Finding: The use of total petroleum hydrocarbons (TPHs) and total polycyclic aromatic hydrocarbons (TPAHs) as dose metrics are not sufficiently predictive of observed toxicity of complex mixtures of oil and dispersed oil (see Figure 3.12). The use of toxic units (TUs) is the only presently available, scientifically sound dose metric.

Finding: Toxicity tests using variable dilution cannot be used to determine if exposure media containing dispersed oil is more or less toxic than is the exposure media containing untreated oil, because (1) dilution changes the concentration of microdroplets in the water-accommodated fractions (WAFs), (2) dilution changes the concentrations of dissolved components in the WAFs, and (3) the concentration dissolved components cannot be estimated from the dilution. By contrast, toxicity tests using the variable loading design can be used to make this determination because the dissolved concentration of the oil components in the WAFs are the same at the same oil loading with or without dispersants.

Finding: Data from high-energy WAF (HEWAF) experiments are difficult to interpret because of the creation of excess microdroplets relative to the dissolved concentrations (see Figure 3.13).

Finding: Data from recent variable loading toxicity tests indicate that dispersed oil is not more toxic than is untreated oil at concentrations below approximately 100 mg oil/L. At concentrations above approximately 100 mg oil/L, the presence of dispersants contributes to increased toxicity (see Figure 3.5). At oil loadings much lower than approximately 100 mg/L, the toxicity hazard posed by dispersed oil does not come from the dispersant itself because the concentrations of dispersants in the toxicity tests are below the acute Hazard Concentration 5% (HC5) (see Figure 3.2).

Finding: The acute and chronic TUs of saturated WAFs for a range of oils, and the chronic and acute HC5, vary over an order of magnitude depending on the composition of the oil (see Figures 3.9 and 3.17).

Finding: The use of passive dosing shows promise for generating exposure media without microdroplets, thereby enabling toxicity testing of dissolved components only. Passive sampling approaches, such as solid-phase microextraction (SPME), show promise for rapid field and laboratory sampling as well. Further standardization of these testing procedures would ensure their interlaboratory comparability and reproducibility.

Finding: Phototoxicity models exist but have not been utilized for determining the contribution of phototoxicity to the overall toxicity of oil in the field.

Recommendation: The use of toxic units should be integrated into revised toxicity testing standards, evaluation criteria for models, and response option risk analysis. This represents a paradigm shift away from developing toxicity tests that attempt to reproduce field exposure conditions and toward developing a consistent means of using toxicity metrics such as HC5 and LC50 for toxicity models used with fate and transport models to compare the exposure and toxicity of various response options, including dispersants.

Recommendation: Recent advances in predictive toxicity models under both lab and field conditions should be incorporated into user accessible tools. The availability of such tools

would facilitate further calibration, validation, and/or refinement as well as support decision making. Future models could include the inclusion of environmental factors (UV light, pressure) and the role of both photosensitization and photomodification on predicted oil toxicity.

Recommendation: Models that simulate the distribution and toxicity of spilled oil need to be validated by comparing their predictions for the same test conditions. Organizations that fund model development should ensure that models, such as PETROTOX and Oiltox, are enhanced and validated through interlab comparisons. As new models evolve for more refined toxicity prediction (e.g., models of phototoxicity), the same should be done. If a future field trial is planned, further validation of these models should be incorporated into the design.

Recommendation: Modify CROSERF protocols so that future toxicity testing data are geared toward informing and validating toxicity models: media preparation, exposure regimes, chemical characterization of exposure media and test species after exposure, and reporting of dose metrics.

Recommendation: Consideration should be given to choosing a number of standardized oil compositions for use as inputs to fate and toxicity model runs. Characterizing these oils into a manageable number of hydrocarbon blocks—consistent with acute and chronic toxicity, phototoxicity, and other more specialized properties—would also be useful.

Recommendation: Funding agencies, research consortia, and other sponsoring groups should require that research teams use standardized toxicity testing methods, such as those developed by the Chemical Response to Oil Spills Ecological Effects Research Forum (CROSERF) program, and analytical chemistry protocols to fully characterize hydrocarbon composition and concentrations in the exposure media. For testing the effect of dispersant, the variable loading test design is recommended.

Recommendation: Improve standardization of oil characterization and composition to provide consistent input that could be coupled with fate and effect models, including lower resolution "fit for purpose" analyses able to quantify oil pseudo-components applicable to trajectory oil spill modeling.

Recommendation: More broadly test the use of passive sampling devices, such as SPME fibers, for real-time field monitoring of dissolved oil exposures and possible toxicity prediction.

CHAPTER 4

HUMAN HEALTH CONSIDERATIONS

INTRODUCTION

Review of Human Health Considerations in Previous National Research Council Reports

Part of the committee's task is to evaluate factors that could affect the decision about the use of dispersants in oil spill response. One of these many factors is the potential impact of dispersant use on human health. While much of the present report builds on the National Research Council's (NRC's) reports (NRC, 1989, 2005), we note that human health considerations were not a focus of these previous studies. The 1989 NRC report recognized the need to consider health hazards in oil spill response decision making, but it did not address the impacts of dispersants specifically. Similarly, one of the limited mentions of human health in the 2005 report identified human health as the first decision point in the dispersant use flowchart (NRC, 2005). In addition, both a mention of potential health effects from 2-butoxyethanol exposure during the *Exxon Valdez* oil spill response[1] and a study assessing the potential for mammalian toxicity were reviewed in that previous report (NRC, 2005).

Overview of Human Health Considerations During and After Oil Spills

While the environmental consequences of marine oil spills has been an important topic of investigation since at least the *Torrey Canyon* and *Santa Barbara* oil spills in 1967 and 1969, respectively, research on the direct and indirect human health impacts of oil spills is relatively recent, whether dispersants were used or not, with some research conducted following the *Exxon Valdez* and *Sea Empress* oil spills but much more initiated after the *Prestige* oil spill in 2002 (Goldstein et al., 2011; Laffon et al., 2016; see Table 4.2 later in this chapter). Furthermore, human health

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[1] The 2005 NRC report contains a comment on page 56 indicating that health effects were found during a previous use of Corexit® 9527. Follow-up by the current committee with a previous committee member indicated that the concern referred to 2-butoxyethanol, a component of Inipol EAP22, a product that was used to promote biodegradation during the *Exxon Valdez* oil spill response. 2-butoxyethanol is also a component of Corexit® 9257.

BOX 4.1
Key Questions

The key questions addressed in this chapter are whether dispersant use alters the health risk imposed by a crude oil spill, either:

1. by dispersant use causing adverse effects;
2. through the potential effects of chemically dispersed oil; or
3. indirectly by changing the extent or duration of the spill and the associated effects.

considerations, which include physical, mental, and social well-being, with regard to dispersant use during oil spills only became a topic of epidemiological investigation during and following the *Deepwater Horizon* (DWH) oil spill (also referred to as the Macondo spill) in 2010 (Kwok et al., 2017a,b; McGowan et al., 2017; Rusiecki et al., 2017). As is emphasized frequently in this report, every oil spill is unique, and decisions about dispersant use that might impact human health will need to take local factors into account for any future spill.

The key questions addressed in this chapter are identified in Box 4.1. In the case of direct adverse effects to response workers, a critical component of the question is whether or not those direct effects can be mitigated through a proper worker health and safety program that focuses on worker training, personal protective equipment, and health and safety monitoring. The committee noted no evidence that the worker health and safety approach would differ for crude oil components whether or not dispersants were present.

With regard to exposure to crude oil, the components of particular concern are the carcinogenic constituents such as the polycyclic aromatic hydrocarbons (PAHs), which are known to cause human lung, bladder, and skin cancer. Additionally, benzene, a volatile component of fresh oil, is known to cause human hematological cancer and is a particular risk to workers who are nearby and may present some concern to downwind communities in close proximity to fresh oil.

A spill can also have an extensive effect in that the presence of surface sheen or of PAHs in seafood can result in prolonged closure of fisheries, which may contribute to secondary effects on community psychological and socioeconomic health and well-being. Worker health and safety is a primary concern during spill response in the United States, and community health, safety, and well-being have also received attention after more recent oil spills. If a response tool such as dispersants can shorten the intensity and duration of response activities, and if the proper worker health and safety and community health and safety measures can be implemented, it would be expected to lessen worker and community health risk. These issues must be examined and weighed as part of the response trade-off decision for dispersant use.

DIRECT HUMAN HEALTH CONSIDERATIONS

The environmental behavior and composition of the spilled oil will largely determine the primary exposure pathways and potential for toxicity in humans, as in other species (see Chapter 3). Primary oil constituents of concern for human health include volatile organic compounds (VOCs), benzene, toluene, ethylbenzene, and xylene (BTEX) in particular, and PAHs. The carcinogenicity of benzene and PAHs, particularly benzo(a)pyrene, are well characterized. In addition, exposure and toxicity of VOC and PAH oil constituents have been reviewed elsewhere (EPA, 1998, 2017; IARC, 2012a,b; Laffon et al., 2016). The use of dispersants may affect the pathways of exposure to oil and oil constituents relevant to human health via changes in the fate, transport, and biodegradation of these oil constituents (see Chapter 2). Here we will focus on published research evaluating the effects of dispersants alone and how they may affect exposure or toxicity of oil constituents most relevant for human health. The committee first covers potential exposure pathways and evidence of exposure, followed by the toxicological evidence that provides information about the intrinsic hazard of a substance (whether, at any dose, the substance could cause an adverse effect) as well as epidemiological evidence from the DWH spill. Risk, a combination of hazard and exposure, is then discussed where sufficient evidence was available (e.g., see the section related to seafood below).

Exposure Pathways for Oil, Dispersant, and Dispersant Oil Mixtures

Dermal and Inhalation Pathways

During an oil spill response, primary response worker exposure pathways of concern are inhalational and dermal exposure to VOC components of oil, including benzene, and potential inhalational and dermal exposure to dispersants or dispersed oil. In addition, air transport of VOCs released from an oil spill can contribute to formation of secondary air pollutants, such as ozone (de Gouw et al., 2011), which could contribute to inhalational exposure to responder and nonresponder populations downwind of the oil spill. For future spills, downwind ozone formation might need to be taken into account during summer months, particularly in regions that are exceeding, or close to exceeding, the primary air quality standard for ozone. Results of modeling of subsea use of dispersants during the DWH spill response suggest a reduction in the VOC inhalational exposure pathway by enhancing the formation of small oil droplets and increasing the dissolution of VOCs within the water column, which also could potentially decrease downwind ozone formation (Gros et al., 2017; see Chapter 2). Aerosolization of oil-containing particles is another potential pathway to both inhalation and dermal exposures (Ehrenhauser et al., 2014; Middlebrook et al., 2012).

Dermal exposure to oil constituents has been shown to cause skin irritation and skin cancer (EPA, 2017), and transdermal absorption will also be an important route in chronic toxicity risk for oil components, particularly related to cancer risk estimates for benzene. Although it is conceivable that the surfactant properties of dispersants may increase transdermal absorption (Subedi et al., 2010), there is limited evidence to determine the effect of dispersants on the transdermal absorption of crude oil components. The likelihood of workers being exposed to a mixture of dispersants and crude oil may be unknown, but it is expected to be low because few responders are in the immediate vicinity when dispersants are applied to surface slicks, either by vessel or aircraft. For responders who could be in the area performing specific tasks, it is expected that appropriate personal protective equipment (PPE) will be used.

While not related to dispersant use, mechanical cleaning of oiled vessels and equipment may splash oil back onto workers; this could result in both inhalation and dermal exposures of oil components and cleaning agents used in the decontamination of oiled vessels or shorelines, particularly if PPE is not used properly.

Ingestion Pathways

Exposure via ingestion could occur through consumption of seafood that may have elevated PAH or dispersant components during or after an oil spill, although protocols for fisheries closures and reopening of waters to fisheries during and after an oil spill are designed to protect public health from this exposure route. These protocols have been in use since the 1989 *Exxon Valdez* oil spill (Yender et al., 2002) and are presented in more detail in the section regarding seafood below; however, how dispersants modulate exposures via this pathway versus the no dispersant alternative has not been systematically evaluated. Another possible route for ingestion of oil components is through poor responder hygiene and possible contamination of food during a response, although this can be addressed by proper training. The use of dispersants could serve to reduce the presence of surface oil and obviate this possible exposure route.

Finally, ingestion by children of dispersed oil that reaches the shore may occur through their hand to mouth habits. Beach closures are designed to minimize this exposure route, although there may be residual oil after reopening. Dispersant exposure, however, is less likely because current policies in the United States restrict dispersant use to beyond 3 nautical miles from shore or in water column depths greater than 10 m. Few field measures exist, but concentrations of dioctyl sodium sulfosuccinate (DOSS) were low (non-detectable to 19 parts per billion [ppb]) in seawater samples taken at beaches during DWH, and spatiotemporal patterns suggested to authors a non-dispersant-related source of DOSS (Hayworth and Clement, 2012). Samples taken at depth during and following DWH (ranging from non-detectable [< 67 ng/L]) to 71 ng/L at 90 m depth to 13,000 ng/L at 1,180 m depth) as well as in weathered oil washed ashore 25-46 months following DWH were also low (~1-260 ng/g) (Place et al., 2016; White et al., 2014). Concentrations of nonionic surfactants in Corexit® dispersants, including sorbitan monooleate (Span 80), sorbitan monooleate polyethoxylate (Tween 80), and sorbitan trioleate polyethoxylate (Tween 85), were found infrequently and at low concentrations (840 to 9,100 ng/L) in seawater (Place et al., 2016).

Exposure Assessment and Guidelines

To date, exposure assessment during oil spills has been hampered by the lack of protocol development for dispersants and, to a lesser extent, for oil component concentrations at baseline and during response activities. Development and validation of an analytical chemistry protocol upfront for monitoring the levels of dispersant (i.e., dispersant components) and chemically dispersed oil in biota, including humans, could allow for monitoring of baseline conditions as well as levels during and post–oil spill, thereby providing a dataset for a more accurate exposure assessment to dispersants and dispersed oil. There would be value in expanding and improving protocols for measuring exposure during a response for oil spill workers (with potential dermal, ingestion, and inhalation exposure routes associated with dispersant application and oil spill response activities) as well as for residents in general (via dermal, ingestion, and inhalation exposure routes from beach activities and/or consumption of seafood). Previous reports have noted the need for emergency responder exposure monitoring and health surveillance (Decker et al., 2013; Reissman and Howard, 2008). The Centers for Disease Control and Prevention (CDC) developed a framework for worker monitoring and disaster research response (CDC, 2018).

A Good Practice Guide was developed to provide very specific, detailed recommendations for worker health and safety as they relate to surface dispersant operations. Protection measures detailed in the guide cover exposures related to breathing aerosol mist, ingestion, absorption through the skin, and splashes to the eyes (IPIECA-IOGP, 2012).

Evidence of Exposure to Crude Oil, Dispersant, and Dispersant Oil Mixtures

Evidence of Exposure to Crude Oil

The human health effects of crude oil are relatively well understood due to occupational health studies of drillers, including those heavily exposed during accidental discharge, in the petroleum refinery workforce, and in industries using crude oil and its components (e.g., EPA, 2017; Macys, 1992). In recent years, studies of workers involved in response after marine oil spills in the United States and elsewhere have reported, with reasonable consistency, respiratory and dermal effects as well as other concerns (see Table 4.2). The committee notes that past studies of petrochemical industry workers have largely been of males, and they likely included fewer women of reproductive age than have been present among the population of oil spill response workers (Bingham et al., 1979). Relatively little information is available concerning other possible vulnerable populations.

Evidence of Exposure to Dispersants

In addition to understanding the impacts of dispersant use on exposure to oil, it is also important to consider whether and how direct exposure to dispersants has implications for human health. Workers involved in dispersant operations, or otherwise in the pathway of dispersant exposure, are presumably most at risk, although the use of appropriate PPE is expected to mitigate this risk (IPIECA-IOGP, 2012). PPE compliance is an important variable and was likely affected in the DWH response due to high ambient temperatures contributing to the discomfort of wearing PPE. While the institution of appropriate workplace protective measures can greatly minimize worker exposure, it is important to understand the potential health consequences of inadequate or inappropriate use of such measures, including unforeseen accidents that lead to human exposure.

Available information about the potential effects (or hazard) of direct dispersant exposure is derived primarily from standard toxicological studies of specific dispersants and of their individual components. Traditionally, one would also look for studies of workers involved in the manufacture of dispersants, but the committee could find no such information.

Two studies of DWH response workers have attempted to disentangle the direct effects of dispersants from other worker health risks. While both studies have noted adverse effects associated with self-reported dispersant exposures, both have significant problems in validating the accuracy of the workers' identification of dispersant exposures (see below). During the DWH spill, personal breathing zone and area air samples were collected on a vessel during and following application of 50 gallons of Corexit® EC9500A. Aerial application of 125 gallons of Corexit® EC9500A co-occurred with the vessel application on the same slick. All substances monitored (including propylene glycol as the component monitored from the dispersant) had either non-detectable concentrations or concentrations well below occupational exposure limits (King and Gibbons, 2011).

Outside of direct exposure through handling or accidental release of dispersants by response workers, contact with the formulated dispersant (i.e., all the components in the ratio present in the product prior to application) is unlikely due to rapid dilution, dissolution, biodegradation, and photodegradation processes.

A more thorough discussion of the fate and transport of dispersants in the marine environment is presented in Chapter 2. The relevant aspects for human health are highlighted here. Dispersant formulations are mixtures of solvents and nonionic and anionic surfactants that have different properties and therefore potential fates in the environment. Once introduced to open ocean waters, dispersant mixtures will be quickly diluted (Lee et al., 2013a) and the various components subjected to degradation processes. Research examining the long-term fate of dispersant mixtures in the environment, however, indicates that DOSS is not always completely degraded. Studies have shown that DOSS persisted for up to 4 years following the DWH spill in oil-sand patties collected from beaches; however, the concentrations of DOSS observed have been extremely low (McDaniel et al., 2015; Perkins et al., 2017; White et al., 2014).

Evidence of Exposure to Chemically Dispersed Oil

In addition to potential direct exposure to dispersants, offshore response personnel working directly with or near dispersant application are the most likely group to be exposed to mixtures of dispersants and crude oil (chemically dispersed oil) via inhalation and dermal pathways, although direct evidence of exposure is lacking. Broader community exposure is significantly less likely, although there may be rare and isolated instances that could lead to ingestion, inhalation, and dermal routes. Again, direct evidence of exposure to chemically dispersed oil is not available from previous oil spill investigations.

Hazard Related to Exposure to Oil, Dispersant, and Chemically Dispersed Oil

Risk is a function not just of exposure but of hazard as well. This section covers the hazard component of risk. Exposure is discussed above briefly and also is covered in subsequent sections. In considering the potential implications of using dispersants in an oil spill, the primary toxicological agents of concern are (1) the individual chemicals in oil and dispersant formulations; (2) the dispersant formulation as a mixture; (3) the mixture of dispersants and crude oil (referred to as chemically dispersed oil here and in Chapter 3); and (4) the weathered chemically dispersed oil.

Toxicological Evidence of Hazard

Crude Oil Toxicity

The potential for acute and subacute dermal toxicity and for the acute central nervous system effects of crude oil components, particularly BTEX, are discussed below. Chronic toxicity concerns of oil constituents are primarily driven by the carcinogenicity of benzene and PAHs via inhalation and ingestion exposure routes, respectively. While the BTEX components have similar acute central nervous system effects, it is only benzene that is a known human carcinogen, causing cancers of the hematological system such as leukemia and lymphoma (ATSDR, 2007; Bingham et al., 1979; Goldstein, 2010a; IARC, 2012a).

Weathered crude oil could account for a substantial part of the exposure of workers and the potential exposures of community members following a marine oil spill if it comes ashore near populations. Far less is known about the potential for human toxicity of weathered crude oil, although lower molecular weight components, including benzene, will be at lower concentrations; and, in the case of extremely weathered crude oils, no bioavailable components may remain. Examination of the effect of weathering on toxicity has been evaluated in other vertebrates relevant to ecological risk assessment (see Chapter 3) and may be relevant for predicting mammalian toxicity.

For comparison, the committee notes that burning of surface oil, another method used in oil spill response, produces pyrogenic PAHs or unsubstituted parent compounds, whereas PAHs found in crude oil are more likely to be alkylated. Jaligama et al. (2015) exposed mice to particulate matter from in situ surface burning of oil during the DWH response and showed induction of pulmonary inflammation. Whether the pyrogenic PAHs provide more or less risk than PAHs naturally present in crude oil is uncertain and warrants further study (Wickliffe et al., 2014; see also Chapter 3).

Dispersant Toxicity

Previous reviews describe the use of dispersant constituents in common household and pharmaceutical agents and summarize available toxicity information, identifying skin, eye, and respiratory tract irritation as the primary acute toxicity endpoints of concern (Dickey and Dickhoff, 2011; Fabisiak and Goldstein, 2011; Fiume et al., 2016; Popovech, 2017). These are similar to symptoms reported in workers and community members following significant oil spills irrespective of dispersant use (see epidemiological evidence section and Table 4.2).

After the DWH oil spill, the National Institute for Occupational Safety and Health (NIOSH) examined respiratory, cardiovascular, and neurotoxicity endpoints following exposure to Corexit®

EC9500A via inhalation and dermal exposure routes in mice and rats. Direct dermal or inhalation exposure may occur over brief periods in the field to workers who venture into spray areas before aerial or boat spray hit the water or to responders spraying dispersants from vessels, particularly if PPE is not worn correctly. Direct dermal exposure to Corexit® EC9500A, including the surfactant DOSS, resulted in allergic contact sensitization in the Organisation for Economic Co-operation and Development standardized Local Lymph Node Assay (EC3 = 0.4% and 3.9%, respectively) and Mouse Ear Swelling Test (Anderson et al., 2011). Acute inhalation exposure (27 mg/m^3, 5 hour) resulted in transient increases in heart rate and blood pressure (Krajnak et al., 2011) as well as changes in biomarkers of neural dysfunction (Sriram et al., 2011); however, breathing rate, airway resistance, and lung inflammation were not altered in these rodent models (Roberts et al., 2011). Repeated inhalation exposures at similar concentrations resulted in no significant long-term changes in cardiovascular or respiratory endpoints (Roberts et al., 2014). George et al. (2001) found gut microbial differences in Fischer rats following a 5-week daily oral exposure to Corexit® 9527, Nigerian crude oil, and a Corexit® 9527 Nigerian crude oil mixture (daily dose volume equal to 0.1% of body weight, 1:20 dilution of crude oil or a 1:50 dilution of Corexit® 9527, or mixture, in peanut oil). No differences in body or organ weight were found across treatment and control groups, and mutagenicity tests were negative. This study was described in detail in the previous 2005 NRC report (NRC, 2005). Limitations of this study include small sample size and unclear relevance of the doses and oral gavage exposure route to expected worst-case doses and exposure routes for humans in field conditions during an oil spill response.

When subsea dispersant use was authorized during DWH, the U.S. Environmental Protection Agency (EPA) Computational Toxicology Program performed rapid toxicity screening to determine which dispersants were least toxic to mysid shrimp and silverside minnow as well as to human cell lines (Judson et al., 2010). For human cell line studies, the LC50 (the concentration that is lethal to half of the cells in culture) for Corexit® EC9500A (120 parts per million [ppm]) was lower than that for several other dispersants but higher than the LC50 determined for another dispersant formulation, Dispersit SPC 1000 (see Table 4.1). It should be noted that the concentrations reported in these studies (the HepG2 assay value of 100+ ppm) are at least one order of magnitude greater than expected field concentrations of dispersant alone (3-10 mg/L depending on application rates; see Chapter 3), and exposures in the field would be expected to be brief. Additional human cell-based studies have examined markers associated with human disease: for example, oxidative stress, mitochondrial dysfunction (Bandele et al., 2012), and chromosomal aberrations in sperm whale skin fibroblasts (Wise et al., 2014). Some dispersant formulations have been evaluated for endocrine-related endpoints: The dispersants Nokomis 3-F4 and ZI-400 had weak estrogenic activity (Judson et al., 2010), and DOSS activated adipocyte (fat cell) differentiation and gene expression in mice, suggesting potential obesogenic activity (Temkin et al., 2016).

During DWH, significant controversy resulted from a comparison of the U.S. Product Schedule dispersant being used to a dispersant approved for use outside the United States. EPA directed studies to compare dispersants. While some other dispersants had lower acute toxicity, they either contained endocrine disrupters or lacked effectiveness in spill response (Coelho et al., 2011a; Hemmer et al., 2011).

Note that dispersant effectiveness varies by formulation and oil composition. Additionally, comparison of dispersant toxicity metrics with those of cleaning agents used in the decontamination of vessels by oil spill response workers may be useful, because surface washing agents, like dispersants, contain surfactants and solvents. As an example, ecotoxicity of cleaning agents used in decontamination, such as PES-51 and Simple Green, has been evaluated by EPA (EPA, 2018). Screening tests in human cell lines, however, as described in Judson et al. (2010) and Table 4.1, were not found for these formulations.

TABLE 4.1 In Vitro LC50s (ppm) for a Variety of Dispersant Formulations and Mammalian Cell Types

Reference	Cell Line	Exposure Time	Corexit® EC9500A	Corexit® EC9527A	Corexit® 9550	ZI-400	Dispersit SPC 1000	Nokomis 3-F4	Nokomis 3-AA	Sea Brat #4	SAF-FRON GOLD	JD 2000
Bandele et al., 2012	Hep2G	72 hr	**275**	**250**	—	**> 400**	—	—	—	—	—	—
Shi et al., 2013	BEAS-2B	24 hr	**200**	**100**	**> 300**	—	—	—	—	—	—	—
Zheng et al., 2014	Multiple w/FBS (w/out FBS)	48 hr	**150 ≥ 200 (16-95)**	—	—	—	—	—	—	—	—	—
Judson et al., 2010	HepG2	24 hr	**120**	—	—	**420**	**28**	**180**	**200**	**410**	—	**> 1,000**
Judson et al., 2010	HEK-298 (AR)	5 hr	**410**	—	—	**670**	**170**	**370**	**200**	**560**	**1,400**	**3,200**
Wise et al., 2014	Sperm whale skin cells	24 hr	**350**	**700**	—	—	—	—	—	—	—	—

NOTES: Corexit® 9550 is no longer on the NCP Product Schedule. Dashes reflect no data available. SOURCE: J. Fabisiak, presentation to the committee.

Chemically Dispersed Oil Toxicity

Limited toxicity studies have been conducted to examine chemically dispersed oil in human cells. These few studies found that cytotoxicity in human lung epithelial cells was greater and gene expression was differentially altered after exposure to chemically enhanced (either by Corexit® EC9500A or Corexit® EC9527) water-accommodated fraction (CEWAF) versus WAF mixtures using Macondo crude oil (Liu et al., 2016, 2017b; Major et al., 2012, 2016; Wang et al., 2012). While important to follow up, these cell culture experiments are difficult to interpret because (1) there is variation in the preparation of the WAFs; (2) the duration of exposures (up to 3 months) is long; (3) the concentrations of dissolved oil constituents were not measured; and (4) there are potential complexities arising from the effects of detergents in the dispersant preparations on cell permeability (Gerhard and Anello, 1969; Jamur and Oliver, 2010; Vinardell and Infante, 1999). Comparing dissolved concentrations of oil constituents is an important component to determining toxicity, as discussed in detail in Chapter 3.

During an oil spill, PAH degradation occurs, in part, through oxygenation at the seawater surface. The extent to which surface application of dispersants could affect the relative uptake into seafood and potential toxicity of oxygenated PAHs is unknown, although a recent study suggested that a relatively persistent PAH, chrysene, when oxygenated, may contribute to the developmental toxicity (heart, circulation, spine, and eye defects, among others, when exposure occurs during development) of weathered oil (Diamante et al., 2017). The net risk is unclear. Similarly, burning of hydrocarbons also leads to formation of benzene, but perhaps not at levels that would counteract the pyrolysis of benzene by the burning of the crude oil.

Epidemiological Evidence from *Deepwater Horizon*

Standard toxicological testing data were available for dispersant components prior to the DWH oil spill. These data, along with the general use of dispersant components in common household and pharmaceutical agents, gave some assurance that the use of a large volume of dispersants in response to DWH could be done safely. However, two studies published in 2017, based on epidemiological analysis of DWH, reported that oil spill response workers who self-reported possible exposure to dispersants had a higher level of symptoms as compared to those who self-reported they were not exposed to dispersants. Both of these studies are described below, and some of the methodological issues that complicate their interpretation are identified.

National Institute of Environmental Health Sciences Gulf Long-Term Follow-Up Study (GuLF) and the Deepwater Horizon *Oil Spill Coast Guard Cohort Study*

As part of an extensive health study of DWH response workers, investigators from the National Institute of Environmental Health Sciences (NIEHS) and collaborative programs attempted to specifically disentangle the impact of potential exposure to dispersants on the previously reported respiratory, dermal, and eye irritation symptoms (McGowan et al., 2017). Between March 2011 and March 2013, 32,608 individuals involved in the oil spill response completed a detailed telephone interview. Of those responses, between 25,659 and 29,648 were judged suitable for further evaluation of the respondents' self-reports of dispersant and oil exposure and contained information about individual symptoms. Less than 10% of the participants claimed exposure to dispersants. Although each respondent was interviewed only once, the authors consider the study to be prospective in nature because the respondents were separately asked about symptoms associated with their oil spill response work and about symptoms within 30 days of the interview period. The adjusted prevalence ratio for all respiratory and eye symptoms was statistically significantly higher during both periods for eye symptoms and for all respiratory symptoms except cough, which was not higher at the time of enrollment. Dermal irritation was reported to be statistically significantly higher for the time of the oil spill response and statistically significantly lower for the interview period. A follow-up study did not find a statistically significant association between lung function at 1 and 3 years after the spill and estimated total petroleum hydrocarbon exposure (Gam et al., 2018a,b).

A somewhat different approach was taken by investigators from the U.S. Coast Guard (USCG) and their colleagues in their cross-sectional evaluation of 4,855 USCG personnel involved in the DWH response (55.8% of total) (Alexander et al., 2018). Of the total responders, 22% were reported to be exposed to dispersant. Each USCG member involved in the oil spill response activity was asked to complete an exit survey, including exposure-related information and symptoms. Using a five-point Likert scale, respondents were asked to quantify how often they were exposed to crude oil/oily water or to dispersants. As in the NIEHS study, the response workforce had a statistically significant greater association for oil plus dispersants as compared with oil alone for the symptoms of coughing, shortness of breath, and wheezing. The USCG survey, though with fewer participants than the number in the NIEHS cohort, consisted of a more uniform group of presumably healthy and trained individuals who filled out a questionnaire in a more proximal time frame (June and November 2010) than did the NIEHS cohort. In addition, one might argue that they were more likely to be knowledgeable about their tasks and the possibility of dispersant exposure. However, valid concerns about recall bias remain as do potential problems related to the unexpectedly low response rate for a uniformed service.

Although the findings would seem to corroborate each other, both sets of investigators recognized that there were many potentially serious confounding issues that could affect their results. This led them to do sensitivity analyses which gave added credence to their findings. However, neither study was able to fully dispel significant concerns about recall bias nor the other problems described below.

Problems Interpreting DWH Dispersant Health Effects Studies

The major problem with these two studies is their limitations in the exposure assessment for dispersants. It was difficult to determine whether, how often, and how much a response worker was exposed to dispersant. Ideally, there would be direct information through biological markers of the extent of exposure, but this was not feasible. Using a questionnaire in which workers were asked to provide information about their exposure is a relatively standard approach, but it requires a reasonable degree of validation. NIEHS has appropriately worked to develop a job exposure matrix for the response workers involved in the GuLF study (Stewart et al., 2018). Unfortunately, they did not have sufficient quantitative information about dispersant exposures. In contrast with total hydrocarbons, for which they developed arithmetic means for the exposure groups and were able to assign ordinal values, for dispersants they depended solely on questionnaire responses (Stewart et al., 2018). The questionnaire used in McGowan et al. (2017) to estimate dispersant exposure of DWH response workers was further complicated by a number of factors.

1. The complex response process. The inherent complexity of the response inevitably led to a confusing set of jobs for the individual worker, many of whom had no previous training. Supervisors were appropriately focused on getting the oil spill response job done quickly and safely, rather than specifically informing the workers as to whether they were potentially exposed to dispersants. Furthermore, there would be little or no difference in what was known about the safe approach to response activities for crude oil whether or not dispersants were present.

2. Delays. Impediments to initiating a human study led the worker response to the questionnaire about dispersant exposure to be significantly delayed, particularly for the NIEHS cohort. This delay eliminated any possibility for the development or use of biological markers of dispersant exposure and complicated worker recall.
3. Recall bias. Recall bias, sometimes called response bias, is inherent in studies of this nature (Coughlin, 1990). It reflects the very human propensity to say yes to questions about potential exposure when experiencing symptoms that are not explained by other exposures, particularly in situations where there is negative publicity about a potential for risk. Concern about recall bias has led many occupational health epidemiologists to avoid discussing potential exposures with those workers who have the adverse effect under study.

Other Studies Potentially Related to Dispersant Exposure

Data from the NIEHS GuLF worker study were also used in studies that further explored mental health indicators (Kwok et al., 2017a) and lung function (Gam et al., 2018a). As each of these studies was dependent for assessment of dispersant exposure on the same questionnaire used in the studies reporting symptoms, the concerns expressed above also apply. As discussed below, there is an opportunity for reanalysis if improved exposure information is forthcoming.

Among those who participated in the oil spill response there was a statistically significant increase in depression (prevalence ratio 1.22, 95% confidence interval [CI] 1.08-1.37) and posttraumatic stress disorder (PTSD) (prevalence ratio 1.35, 95% CI 1.07-1.71). However, no statistically significant increase was observed in the group labeled as “any self-reported work with dispersants” (depression prevalence ratio 1.04, 95% CI 0.92-1.19; PTSD prevalence ratio 1.15, 95% CI 0.91-1.45) (Kwok et al., 2017a).

Lung function was studied by spirometry during home visits occurring between May 2011 and May 2013. No differences were found between workers and nonworkers. Among response workers there were small but statistically significant reductions in lung function among those involved in decontamination or with high exposure to burning oil. In comparison to other workers, those who were believed likely to have had exposure to dispersants had modestly lower forced expiratory volume 1 (FEV1), forced vital capacity (FVC), and FEV1/FVC measurements. The subcohort that reported personally using dispersants (in contrast to being on a vessel that used dispersant) was reported to have a suggestive inverse association with FEV1/FVC (Beta –0.76%; 95% CI –1.33 to –0.18). But no difference in lung function measurements was found across tertiles of dispersant exposures (Gam et al., 2018a).

A series of studies by D’Andrea and Reddy (2013, 2018) claim longer-term effects on a variety of organ systems in workers exposed to crude oil and to dispersants as compared to a control group. Insufficient information is available to fully assess the implications of these studies as they do not conform to standard epidemiological methodology (Piacentino et al., 2014). Questions about these studies are also raised by internal inconsistencies in the hematologic findings in relation to the potential for the alleged benzene effects as well as by the reported presence of an increase in a benzene biomarker (urinary phenol) well past the time that this biomarker would persist in the body following the cessation of response work.

Next Steps for DWH Analyses and Considerations for Future Work

The information from studies of DWH response workers suggests the need for continued diligence in avoiding dispersant exposure during any future use. An impressive amount of exposure analysis has been performed, but there may be existing data sources that could help pinpoint who was exposed and under what conditions, thereby improving an understanding of the potential role of dispersants in producing the health effects reported in DWH responders.

Such continual evaluation, alone and together, of the USCG and NIEHS cohorts merits consideration, as it may help future decision makers determine whether to use dispersants. Furthermore, lessons learned from the methodological limitations of the DWH studies could be applied to future studies of dispersant use. Also, it appears that public health advice would be helpful to the On-Scene Coordinator. The Safety Officer position has historically been filled by someone who has occupational health and safety expertise, and this position remains a critical part of the response for worker health and safety. The Assistant Safety Officer for Public Health position is key to developing liaisons with local public health authorities in complex oil spills (USCG, 2014). However, the human health complexities in events such as the DWH oil spill go beyond the response workers and communities impacted by the event. Approaches such as a Spill Impact Mitigation Assessment are available to assess potential trade-offs associated with such a wide-ranging emergency response (see Chapter 6).

Additional information from the two existing studies associating self-reported exposure to dispersants with symptoms in response workers could be acquired through coordination and exchange of information among USCG and NIEHS scientists. As some workers appear to have been included in both studies, the two groups of investigators could assess the extent to which their findings for these workers corroborate each other. After-action reports related to dispersant usage, including releases, provide information useful to identifying workers potentially exposed to dispersants (Houma ICP Aerial Dispersant Group, 2010). Appropriately designed exposure-related studies require and may deserve significant research funding.

Workers involved in a large-scale crisis response effort start with the initial response group who have a certain level of experience in spill response and may have been screened for health-related requirements of the job. The remainder of the response pool are pulled from a general population who may have no previous experience in spill response work. They are provided with preemployment training, such as the Occupational Safety and Health Administration's (OSHA's) Hazardous Waste and Emergency Response standard or other just-in-time training and deployed to the scene of the event. Some of these workers may have preexisting health conditions that are not evident because there is no requirement for a preemployment physical or no baseline health data was collected or made available by the worker (NIEHS, 2012). In considering dispersant use, proper exposure assessment and toxicological evaluation would recognize that response workers may not be from a healthy worker population and may not know how to minimize exposure.

The two recently released DWH worker health studies have suggested that exposure to dispersants contributes to the symptoms of oil spill responders, particularly of the respiratory tract. If confirmed after more detailed exposure assessment, or in subsequent studies of response workers, it is important to determine whether longer-term consequences will follow, as has occurred, for example, in the 9/11 response group (Mauer et al., 2010). Relevant agencies, including the National Academies Gulf Research Program, could consider a request for applications aimed at understanding how a dispersant, as differentiated from crude oil components alone, might potentiate the effects of a pulmonary irritant or otherwise be responsible for the observed association.

The committee briefly considered possible biophysical mechanisms that might account for the seeming greater effect on respiratory symptoms of dispersant plus oil than oil alone, if in fact such occurs. These potential mechanisms ranged from a dispersant effect on airway protective systems, allowing greater penetration of irritants derived from oil, to an interactive effect with the salt-induced cough not uncommon in workers in coastal beach areas during summer. Research into understanding these mechanisms conceivably could have the benefit of identifying a characteristic of dispersants that is responsible for toxicity, if it occurs, but not of particular value for its desired dispersant effect, thus allowing the formulation of a less toxic dispersant.

Improving the exposure analysis for the NIEHS and USCG studies could be emphasized by both the NIEHS and USCG groups. This could include meeting together to understand the extent to which individual workers may be enrolled in both studies and, if feasible, the extent to which the exposure estimates are replicable. Continued analysis of data sources allowing better location of workers in relation to sources—including better understanding of who was exposed and under what circumstances and duration—would be useful. Further clarification as to whether subcontractors responsible for dispersant applications are part of either study—and, perhaps, could be singled out as a high dose comparison group—could be a next step. In view of the uncertainties surrounding identification of workers exposed to dispersants by the NIEHS and USCG groups, consideration could be given to reevaluating the available information concerning dispersant usage in relation to the reports of these same workers' symptoms available to those conducting the NIEHS and USCG epidemiological studies of dispersants.

Epidemiological Evidence from Studies of Other Previous Oil Spills

Previous Oil Spills (Exxon Valdez, MT Braer, Sea Empress, MT Erika, Prestige, MT Hebei Spirit)

Studies evaluating human health outcomes during and following previous oil spills have been reviewed (Aguilera et al., 2010; Goldstein et al., 2011; Gräbsch, 2016; Laffon et al., 2016). Here the committee provides a summary table of human health studies conducted following oil spills when dispersants were used versus when they were not.

In general, studies published on physiological effects have identified a broad spectrum of acute health symptoms (respiratory, dermal, eye and throat irritation, headache, nausea, vomiting/dizziness, and injuries and back pain) associated with exposure and/or response to oil spills (see Table 4.2). In addition, studies published following the *Prestige* accident also found increases in airway injury and in chromosomal damage in fishermen who participated in response activities versus fishermen who did not participate (Rodríguez-Trigo et al., 2010). Gräbsch (2016) presents a comparison of human health study findings following the *Prestige* and *Hebei Spirit* oil spills as two relatively well-studied oil spills, where chemical dispersants were applied (*Hebei Spirit*) versus not applied (*Prestige*). Direct exposure to dispersants was not evaluated. Frequency of acute symptoms—including eye (14% versus 20%), respiratory tract irritation (23% versus 39%), and headache (13% versus 36%)—self-reported by oil spill workers within the first 2 weeks after the spills were lower during the *Prestige* versus *Hebei Spirit*, respectively. Dispersant use was only one of many differences between these oil spills, and the type of oil and differences in the response population are also likely important explanatory factors for the differences in health symptoms experienced (Gräbsch, 2016).

In 2015, the German Federal Institute for Risk Assessment held a workshop to address the potential for dispersant use as an oil spill response in German waters. A publication derived from the workshop in its review of the evidence related to health effect concludes: "A reliable assessment of the overall impact of dispersant use on human exposure and potential health impairment is still needed," which describes the goal of this chapter (Grote et al., 2018).

Seafood Exposure Considerations

Alteration in PAH Uptake in Fish, Crustaceans, and Bivalves

PAHs are a chemical class that contains known human carcinogens, and they are present in varying amounts in crude oil. The uptake of PAHs in fish and shellfish and subsequent ingestion is an important route of potential human exposure during and after an oil spill. Fisheries are generally closed if an oil sheen is detected at the surface, in part because navigation through this area may

TABLE 4.2 Studies Examining Human Health Outcomes During and After Oil Spills[a]

Oil Spill	Year	Amount (Kt) and Type of Oil Released	Amount (T) of Chemical Dispersant Used	Human Health Outcomes Evaluated	Methods	Findings	References
Oil spills in which chemical dispersants were used and human health outcomes were evaluated							
Exxon Valdez	1989	37, crude oil	Aerial application trials only took place over several days shortly after the spill and before the majority of response workers were on scene (Gilson, 2006)	Mental health	Cross-sectional and longitudinal, survey	Increased generalized anxiety disorder, depression, PTSD, heightened effect on Alaskan Natives and subsistence lifestyle	Arata et al. (2000); Gilson (2006); Palinkas et al. (1993a,b); Picou et al. (1992)
MV Braer	1993	85, crude oil	120 Although most of the dispersion that occurred was due to sea state and the type of oil	Lung function, VOC exposure, acute illness symptoms, liver and renal function	Cross-sectional, survey, spirometry, urinary biomarkers of exposure, blood liver and renal function, DNA damage in peripheral blood	Increased headache, sore throat, itchy eyes, no significant differences in lung, renal or liver function, toluene urinary metabolite heightened, no differences in DNA damage measures	Campbell et al. (1993, 1994); Cole et al. (1997)
Sea Empress	1996	72, light crude oil	445	Acute illness and mental symptoms	Cross-sectional survey, retrospective cohort	Increased headache, sore throat, anxiety, depression	Gallacher et al. (2007); Lyons et al. (1999)
Nakhodka	1997	6, heavy oil	Limited amounts sprayed by helicopter	VOC exposure, acute illness symptoms	Survey, personal air monitoring, urinary biomarkers	Increase in urinary marker for toluene exposure, headache, eye and throat irritation increased	Morita et al. (1999)
Tasman Spirit	2003	35, light crude oil	16	Acute illness symptoms, lung function	Cross-sectional, spirometry, and survey	Lower lung function, increased ocular and respiratory symptoms	Janjua et al. (2006); Meo et al. (2008, 2009a,b)

Hebei Spirit	2007	10, Middle Eastern crude oils	298	Acute illness symptoms, lung function, VOC and PAH exposure, oxidative stress biomarkers	Longitudinal, cross-sectional, survey, urinary biomarkers	Headache, eye and throat irritation increased, lung function decreased, some differences in urinary exposure biomarkers after spill response versus before, but no association with physical symptoms, oxidative stress biomarkers increased and correlated with PAH exposure biomarker 1 year after cessation of response efforts	Cheong et al. (2011); Ha et al. (2012); Jung et al. (2013); Lee et al. (2010); Noh et al. (2015)
Deepwater Horizon	2010	500-750, LA sweet crude oil	~4,050 surface ~2,900 subsea	Acute illness symptoms, VOC exposure	Longitudinal, survey	See above detailed summary	See summary above
Oil spills in which chemical dispersants were not used and human health outcomes were evaluated							
Erika	1999	20, heavy fuel oil	N/A	Acute illness symptoms	Cross-sectional survey	No control group	Schvoerer et al., 2000
Prestige	2002	63, heavy fuel oil	N/A	Acute illness and injury symptoms, lung function, biomarkers of airway injury, mental health, DNA damage in peripheral blood	Cross-sectional survey, cohort of response workers	Increased headache, sore throat, dizziness; elevated markers of airway injury at 2 years but not 6 years after response work; conflicting reports on mental health; increased micronuclei (indicator of DNA damage) in peripheral blood	Carrasco et al. (2007); Pérez-Cadahía et al. (2008a,b); Rodrigues-Trigo et al. (2010); Sbucedo et al. (2009, 2010); Suarez et al. (2005); Zock et al. (2012, 2014)

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[a] Table was developed based on compilation of information in similar tables found in CRRC Dispersant Initiative Final Report (CRRC et al., 2012), Goldstein et al. (2011), Gräbsch (2016), and Laffon et al. (2016),. Different sources may give somewhat different amounts of oil spilled or dispersants used.

result in contamination of fishing gear on vessels (nets, holding tanks, etc.). Reopening waters to fisheries typically requires seafood tissue analysis of PAH levels, ensuring that they do not exceed exposure limits based on cancer risk levels (NOAA/FDA, 2010; Yender et al., 2002). Cessation of fishery activities can have a significant effect on the overall economic, psychosocial, and health impacts of any major oil spill. The extent to which PAH concentrations in seafood can be altered by the use of a dispersant is central to any decision about its use or about comparing its use with other response methods.

Dispersant Constituents in Seafood

Because analytical strategies had not been developed, reports of dispersant constituents found in seafood were not compiled during and following oil spills prior to DWH. Due to public concern over the use of dispersants during the DWH response, the National Oceanic and Atmospheric Administration (NOAA) and the U.S. Food and Drug Administration (FDA) developed a protocol using LC MS/MS for determination of DOSS (CAS 577-11-7)—a component of Corexit® EC9500A, Corexit® EC9527A, and other commercially available products—in seafood samples (Flurer et al., 2010). FDA and NOAA finalized methods for detection of DOSS on October 27, 2010, approximately 6 months after the initial blowout. DOSS was chosen in part because it could be distinguished from oil-related compounds and because of its bioactivity, low volatility, and potential to persist in the environment compared to other dispersant components (Lubchenco et al., 2012; Ylitalo et al., 2012). DOSS is widely used in over-the-counter medications and other products to which humans are frequently exposed, suggesting that it is generally harmless at ingestion doses of up to 0.1 mg/kg body weight per day, which is based on weanling weight loss in reproductive toxicity studies conducted in rodent models (FAO/WHO, 1991, 1995). Petroleum-derived solvent components (e.g., petroleum distillates, CASRN 64742-47-8) of dispersants could also be considered in toxicity evaluations. A full component list of Corexit® EC9500A and EC9527A, the two dispersants used during the DWH response, can be found in Chapter 1.

Results from subsequent laboratory testing of a variety of commercially relevant species (Benner et al., 2010) and in field testing following DWH suggest minimal potential for bioaccumulation in seafood or exposure to DOSS via ingestion of seafood (Ylitalo et al., 2012). Of the > 8,000 seafood samples (including oysters, shrimp, crab, and finfish) that were submitted for chemical analysis by NOAA/FDA between June 2010 and March 2011, 393 were retrospectively tested for DOSS and 14 had detectable levels of DOSS which ranged from 0.011 to 0.41 μg/g (Dickey and Dickhoff, 2011). The concentrations detected were well below the derived level of concern (LOC) of 100-500 μg/g, which assumes a 70 kg person eating approximately 10-50 g of seafood per day for 5 years. Additional analyses of finfish and shrimp after reopening of waters to fisheries after DWH did not detect DOSS in seafood samples, and risk estimates, even for high consumers, were low (Fitzgerald and Gohlke, 2014; Sathiakumar et al., 2017; Wickliffe et al., 2014; Xia et al., 2012).

The additional step of developing methods for dispersant detection during an active emergency response resulted in a lack of baseline information and estimates of exposure during the spill; this could be avoided by moving this activity to the preplanning phases of oil spill response efforts. It is uncertain whether findings would be similar for other dispersant components or formulations or for an oil spill response that relies more or less on surface versus subsurface dispersant application, because detection would be dependent on potential differences in fate, transport, biodegradation, metabolism capabilities, and other factors.

Polycyclic Aromatic Hydrocarbons Concentrations in Seafood

Closure of federal waters to fisheries during and following an oil spill requires coordination between FDA, which is responsible for regulation of contamination or taint of seafood destined for interstate commerce, and the National Marine Fisheries Service of NOAA, which is responsible for regulation of fisheries commerce. Visible presence of surface sheen and oil trajectory modeling is used to make closure decisions. Direct toxicity of oil and dispersant to marine life is discussed in Chapter 3. Following a fisheries closure based on an environmental assessment (NMFS, 2010), agencies develop risk-based reopening criteria for species of concern and implement a seafood tissue sampling and analysis plan (Yender et al., 2002).

Protocols for reopening fisheries after closure from an oil spill have been based on cancer and noncancer human health risks associated with PAH concentrations in muscle tissue of a variety of seafood evaluated through sensory testing (Reilly and York, 2001) and chemical analysis via gas chromatography–mass spectrometry or liquid chromatography-fluorescence (Gratz et al., 2010; Sloan et al., 2004). More rapid analytical techniques are under development (Rusina et al., 2017). As described above, during the reopening of fisheries after DWH, an additional risk-based criterion for the dispersant component DOSS was developed.

Standard risk assessment calculations are completed to determine the acceptable concentration in seafood tissue and are referred to as the LOC. A variety of assumptions are made considering average and high-end consumption rates of each type of seafood, acceptable risk level for carcinogens, exposure duration, and age sensitivity (Dickey, 2012; Gohlke et al., 2011; Klasing and Brodberg, 2013; NOAA/FDA, 2010; Rotkin-Ellman et al., 2012). Calculated LOCs have varied considerably across oil spills primarily driven by differences in the choice of risk level and exposure duration (Gohlke et al., 2011).

The following 13 PAHs and their alkylated homologs have been considered in the risk evaluations during previous oil spills: naphthalene, fluorene, anthracene, phenanthrene, pyrene, fluoranthene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benz[*a*]anthracene, indeno[1,2,3-*cd*]pyrene, dibenz[*a,h*]anthracene, and benzo[*a*]pyrene. Similar to the toxic unit dose metric described in Chapter 3 (Equation 2), the cancer LOCs are based on the summation of benzo[*a*]pyrene equivalents (BaPE) for 7 PAHs (chrysene [0.001], benzo[*b*]fluoranthene [0.1], benzo[*k*]fluoranthene [0.01], benz[*a*]anthracene [0.1], indeno[1,2,3-*cd*]pyrene [0.1], dibenz[*a,h*]anthracene [1], and benzo[*a*]pyrene [1]); the following equation is used to establish a LOC in seafood:

$$\text{LOC (BaPE)} = (RL \times BW \times AT \times CF) \div (CSF \times CR \times ED),$$

where the risk level (*RL*) has been set at 1×10^{-6} or 1×10^{-5}; body weight (*BW*) is 12 to 80 kg based on average child or adult body weight; averaging time (*AT*) has been set at 70 or 78 years based on average life expectancy; and the unit conversion factor (*CF*) = 1,000 µg/mg. The cancer slope factor (*CSF*) has been set at 1.7 or 7.3 mg/kg/day based on EPA's BaP risk assessment for oral exposure (EPA, 1994) and are derived from dose-response data on gastrointestinal cancers in rodent models. The seafood consumption rate (*CR*) has been set at various levels for different oil spills. For example, for the DWH spill, 13 g/day for shrimp and crab, 12 g/day for oysters, and 49 g/day for finfish were used based on 90th percentile seafood consumers in the 2005-2006 National Health and Nutrition Examination Survey study. It is important to note that PAH exposure via consumption of seafood will also vary based on culinary practices and preparation methods (dos Santos Fogaca et al., 2018). The exposure duration (*ED*) has been previously set to 2, 5, 10, or 70 years, based on estimates of the retention period of PAH contamination in seafood.

These exposure duration estimates are conservative and generally based on retentions seen in those species that cannot readily metabolize PAHs, such as oysters, which have less efficient metabolic capabilities for PAHs when compared to fish or crustaceans (Varanasi, 1989). As an example, the last reopening of Louisiana state waters in Barataria Basin after the DWH spill was in June 2015, more than 5 years after the blowout, due primarily to the entrainment in sediments and retention of PAHs in oysters (LDWF, 2015).[2] The calculated LOCs for the DWH spill were 35 ng/g (ppb) BaPE for finfish, 132 ng/g (ppb) BaPE for shrimp/crab, and 143 ng/g (ppb) BaPE for oysters. In addition, one area off the Louisiana coast was reopened, then closed again to fishing for red royal shrimp, due to a shrimper reporting tarballs in his nets while trawling for this sediment dwelling species.

Determination of noncancer risks has been based on EPA reference dose calculations (*RfD*; an estimate of a daily exposure of each chemical that likely has no significant risk during a lifetime) for the six additional PAHs (naphthalene, fluorene, anthracene, phenanthrene, pyrene, and fluoranthene) using the following equation:

$$\text{LOC} = (RfD)(BW)(CF) \div CR.$$

Oral *RfD*s used are from EPA's Integrated Risk Information System: 0.02 mg/kg/day naphthalene, 0.04 mg/kg/day fluorene, 0.30 mg/kg/day anthracene/phenanthrene, 0.03 mg/kg/day pyrene, and 0.04 mg/kg/day fluoranthene, and they are based on neurotoxicity and developmental toxicity. *BW*, *CF*, and *CR* are defined as above for the cancer risk assessment. The calculated LOCs ranged between 49.0 µg/g (pyrene in finfish) and 2,000 µg/g (anthracene/phenanthrene in oysters) for DWH. Because noncancer LOCs are much higher than those calculated for carcinogenic PAHs, LOCs derived from the carcinogenic PAHs typically drive the assessment.

Considerable uncertainty exists in RfDs, cancer classifications, CSFs, and equivalency factors, creating variation in risk-based criteria for fisheries reopenings seen across state and federal agencies and over time (Gohlke et al., 2011). For example, the calculated acceptable concentration of BaPE for finfish required for reopening following the *Exxon Valdez* oil spill were set a 0.5 ppb; whereas the LOCs set for finfish after more recent spills, including *Cosco Buscan*, *Dubai Star*, and DWH, were almost two orders of magnitude higher (35-44 ppb). Application of different acceptable risk levels (1 in 1 million versus 1 in 100,000 or 10,000) and different exposure durations (5 to 70 years) accounts for a large portion of the variation; however, differences in other parameters are also notable. For example, the California Environmental Protection Agency considers naphthalene and its alkylated homologues in their cancer risk determination. In addition, equivalency factors and CSFs have changed over time as the toxicological and epidemiological data are reassessed. Moving forward, as the body of evidence becomes more refined, risk-based criteria for fisheries reopenings should become more consistent in the evaluation of health risk associated with chemically dispersed oil and inclusion of seafood contamination risks into integrated models.

Additional Considerations in Comparing Toxicity Across Response Methods

The ultimate decision to use dispersants will be made by an agency different from the one with statutory responsibility for evaluating seafood safety and closure decisions. Therefore, close coordination would be useful to provide valuable information about consideration of the various factors.

If dispersants are used, the reopening protocol could be modified to include risk-based criteria for dispersant components, such as DOSS, in addition to PAHs. In addition, use of dispersants may affect the species of concern determined in the reopening protocol, because species in the water column may have increased exposure. The sampling and analysis plan may be altered to

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[2] See https://web.archive.org/web/20190801090052/http://www.wlf.louisiana.gov/news/39225.

reflect differences in the species of concern, potential for more rapid biodegradation, and increased complexity of the distribution of the dispersed oil. The estimated exposure duration may be altered by dispersant use and could be considered in the risk-based LOC calculations once further information is gathered. The waiting period that was used following the DWH was set at 30 days of no visible surface oil. A more effective reopening protocol may consider subsurface and sediment measurements in addition to tissue samples; for example, following the DWH spill there was a closure for red royal shrimp, then reopening, and then reclosure (NOAA, 2011).

Whether dispersant use alters the fate and transport of trace metals found in oil and, ultimately, concentrations found in seafood, is not well understood (Joung and Shiller, 2013; Liu et al., 2012; Steffy et al., 2016). Oil-related trace metal (vanadium, mercury, nickel) concentrations in oysters and sediment were found to be within historically observed ranges for most sites evaluated post-DWH as part of NOAA's National Status and Trends Program (Apeti et al., 2013). Vanadium and nickel concentrations were elevated in sediment and oysters post–oil spill at some sites, and concentrations were below human health levels of concern. An analysis of whale tissue showed elevated chromium and nickel concentrations post-DWH (Wise et al., 2014). FDA surveillance of shrimp, crab, and oysters and an analysis of reef fish did not indicate elevated mercury, cadmium, lead, or arsenic tissue concentrations post-DWH (FDA, 2011; Fitzgerald and Gohlke, 2014).

Alteration in Benzene, Toluene, Ethylbenzene, and Xylene Exposure

Neurological and carcinogenic impacts from inhalation of VOCs are a primary consideration in establishing acute and chronic inhalation exposure guidelines to protect response workers. Volatile aromatic hydrocarbons, often considered together as BTEX, all have similar central nervous system anesthetic-like effects that are additive. Studies demonstrating more subtle effects on coordination—akin to mild alcohol intoxication (Benignus et al., 2011)—suggest that VOC exposures can affect coordination and judgment in ways that might increase the likelihood of injuries and accidents among response workers. Benzene is a known human carcinogen present in crude oil. It causes acute myelogenous leukemia and other hematological cancers (ATSDR, 2007; Goldstein, 2010a; IARC, 2012a). The NIOSH Immediately Dangerous to Life or Health (IDLH) value, usually based only on a 15-minute averaging time, is 500 ppm for both benzene and toluene, 800 ppm for ethyl benzene, and 900 ppm for xylenes. For example, at 300 ppm some decrease in central nervous system function that could impair safe decision making could be expected, particularly as BTEX blood levels would accumulate during the 1-hour period. Without effective PPE, it would not be particularly surprising if response workers were "woozy" after a few minutes of exposure. Contributing to the central nervous system effect would be aliphatics, which presumably would be a significant part of the VOC measurement: for instance, the IDLH for octane is 1,000 ppm and for pentane 1,500 ppm.

Based on carcinogenicity, the permissible occupational exposure limit for benzene is 1 ppm as an 8-hour time weighted average, with a maximum short-term exposure limit of 5 ppm for any 15-minute period (Substance Safety Data Sheet, Benzene, Standard Number 1910.1028 App A). The benzene standard also outlines under what conditions workers are required to wear and be trained in the use of PPE. As has been recognized by OSHA, their standards for other volatile aromatic hydrocarbons, including toluene, ethylbenzene, and xylene, are out of date, and they often exceed industry and state guidelines The NIOSH Recommended Exposure Levels (100 ppm), which are also published by OSHA, are those that are generally followed and are listed in the Annotated OSHA Z-2 Table along with the Cal/OSHA Permissible Exposure Limit (10 ppm) and the American Conference of Governmental Industrial Hygienists' Threshold Limit Value (20 ppm) (OSHA, 2018).

In contrast to PAHs, BTEX chemicals are highly volatile, possess some solubility in seawater, and degrade relatively rapidly in the atmosphere—with the rate of degradation being dependent on temperature and on the presence of active species of oxygen generated in the atmosphere, through sunlight at the water surface, or through biological processes. Benzene is readily measurable in air or water.

Public concern about the potential for leukemia due to an oil spill can be anticipated to result in a focus on benzene measurements, as occurred following DWH, which leads to estimation of the extent to which a marine oil spill results in worker and community exposure to benzene. Using standard risk assessment techniques, benzene in air can readily be converted into lifetime risk estimates of leukemia for exposed workers or community members.

In the DWH response, one rationale for subsea dispersant injection (SSDI) at the crude oil release point and surface application at the wellhead was that they would increase dispersion and enhance dissolution of the more volatile portion of the crude within the water column, thereby reducing potential VOC exposure and fire hazards for response workers at the surface near the wellhead (USCG, 2011). Indeed, subsequent modeling suggests that SSDI may decrease overall VOC levels at the surface (Gros et al., 2017). Personal samplers worn by response workers during DWH response (from late May through July 2010) and analyzed for BTEX resulted in very few samples above detectable limits, and none approached the health limits (King and Gibbons, 2011; OSHA, 2018). These data suggest that response workers were not subjected to high-exposure conditions during SSDI; however, no published personal exposure data were available to the committee to assess exposure prior to initiation of SSDI in mid-May 2010 beyond what is mentioned above. The On Scene Coordinator Report also mentions recorded VOC levels above 200 ppm (USCG, 2011).

Field trial studies of surface application suggest that the dispersant Corexit® EC9500A and the surfactant Span 80 may increase aerosolization of less volatile oil constituents, such as PAHs, which would also need to be considered in evaluating exposure to response workers, although atmospheric concentrations at relevant distances away from dispersant application exclusion zones are expected to be low (Ehrenhauser et al., 2014; see Chapter 2, aerosolization section).

INDIRECT HUMAN HEALTH CONSIDERATIONS

The literature from various oil spills around the world, including DWH-related studies, consistently report adverse health effects among response workers and, more infrequently, have measured adverse health consequences in affected community members (see Table 4.2). Adverse community health effects often, but not always, have been associated with psychosocial and socioeconomic impacts on the community rather than toxicity associated with direct exposure to chemicals or crude oil. Communities at particular risk are those that already have relatively poor health and a past history of possible environmental injustice, which characterizes many members of the communities affected by the DWH oil spill (Hansel et al., 2017). These various health impacts in workers and community members are likely at least partly dependent on the duration of the oil spill recovery period. To the extent that dispersants fulfill expectations and shorten this duration, this presumably would lessen the overall impacts on worker and community health. A more detailed discussion of response worker injury risk from the DWH spill and duration of response activities is below.

As one reviews the extensive data collected during DWH, there is injury and illness information by time period, location, and type of injury, but there is no specific breakdown of the difference between injuries and illnesses associated with dispersant use versus without dispersant use (see Figure 4.1). Of the 2,129 total response worker injuries and illnesses recorded between April 23 and July 27, 2010, 32% were offshore. The most common injuries reported were sprains and

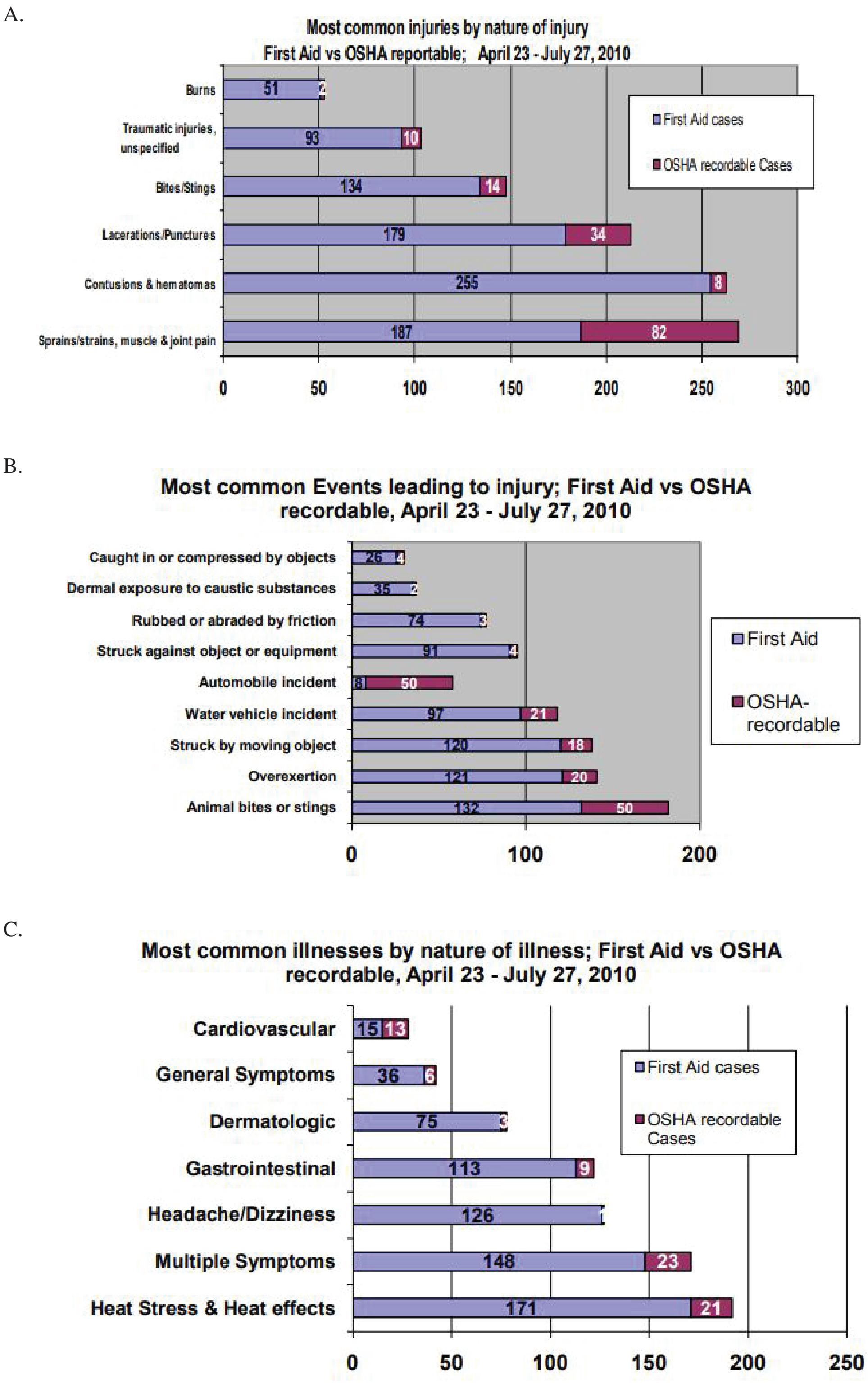

FIGURE 4.1 Reported cases of injury and illness between April 23 and July 27, 2010. SOURCE: CDC.

strains, contusions, and lacerations or punctures. The most common events leading to injury included animal bites and stings, whereas dermal exposure to caustic agents accounted for a small portion of reported events leading to injury (see Figure 4.1B). For illness reporting, dermatologic and headache/dizziness were commonly reported, with multiple symptoms and heat stress being the most common reported illnesses (see Figure 4.1C). While the data suggest that exposure to chemicals (e.g., from dispersants, oil, or other agents used in response work) may account for at least some of the reported injuries and illnesses (see Figures 4.1B and 4.1C), the lack of details in this dataset makes it challenging to draw any conclusions for comparing dispersant use as a response tool compared with other response tools, such as in situ burning or mechanical removal. Many response methods were employed simultaneously during the spill. There is also potential for exposure to many different chemicals during oil spill response, and specific chemical exposures are not identified in this dataset.

This lack of detail in responder health surveillance is not specific to oil spill response. The National Response Team Emergency Responder Health Monitoring and Surveillance Technical Assistant Document dated January 26, 2012, notes that even though lessons learned from previous emergency events continue to be applied, "there are still significant gaps and deficiencies in health monitoring and surveillance for emergency response workers." The report further points out a need "for a coherent, comprehensive approach to protecting these groups of workers and for detailed, practical guidance on implementing such an approach."

Oil spill response carries certain risk for workers, especially in the emergency response phase. Large and complex spills generally require a large number of people and, depending on the situation, may require long work hours. In a recent nationwide study, working in jobs that require overtime was associated with a 61% higher injury hazard rate relative to jobs that do not require overtime (Dembe et al., 2005).

If the use of dispersants might alter the response time and duration of the response, this risk-benefit analysis and possible change in injury hazard reduction rate can be part of the decision analysis. Duration of the hazard is a major determinant of risk. A question central to determining the impact of dispersant use on human health risk is whether and to what extent it shortens the response period and the return to normal. If use of dispersants shortens the number of days needed for response and/or number of workers needed for response, then theoretically this would result in less occupational injury risk (e.g., less likelihood of slips and falls in a tired group of response workers) associated with an oil spill response. In the case of DWH, the committee did not have sufficient information available to determine whether or not the use of dispersant altered the duration of the effects.

Weighing occupational health risks and benefits associated with use of dispersants during oil spill response should include an examination of the value of dispersant application subsea in improving the occupational safety of response workers working in the vicinity of the source control. Although the most appropriate goal for occupational health and safety is zero adverse events, it is not unreasonable to utilize comparative data on adverse health and safety events to help evaluate health and safety activities. During the DWH spill and response activities, the illnesses and injuries were coded and categorized using the Bureau of Labor Statistics Occupational Injury and Illness Classification System (NIOSH Illness and Injury Data[3]). However, more directly relevant record-keeping on worker health and safety related to the spill response itself, with the possibility of more direct evaluation of potential exposure to dispersant and dispersed oil, should serve as the baseline metric for evaluation of response for future oil spills.

Improving on the details of injury and illness reporting for worker health and safety would be useful for the next oil spill, including a clear focus on whether workers were exposed to disper-

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[3] See https://www.cdc.gov/niosh/topics/oilspillresponse/data.html.

sant. To that end, publication and ready availability of well-defined DWH worker health and safety statistics would be helpful.

Duration of Oil Spill Response Activities

Several previous studies have characterized significant economic, psychosocial, and mental health effects during and after oil spills in coastal communities (see Table 4.2). It is reasonable to expect that should there be a shortening of a spill response, then improvements in community resilience would be expected. The economy and community well-being would be improved with people getting back to their normal work and leisure routine, fisheries and related industries reopening, and tourism returning to its normal state. The positive impacts of more rapid response periods vary, and may include a shorter duration of direct economic impact, should fisheries closure times be shortened (NMFS, 2010). Other potential positive impacts may include the value of a restored natural environment and improved mental and behavioral health.

An effort could be made to compute the value of use of dispersants versus nonuse as it relates to the duration of the spill response. This should include the impact on the estimated time component of the risk of seafood PAH contamination. If the use of dispersants is shown to shorten the duration, then presumably this would lessen the impact on overall community health and well-being and provide a significant benefit from a Spill Impact Mitigation Assessment perspective (see Chapters 1 and 6).

Risk Communication and Transparency

Impact of Dispersant Information Availability

The importance of the transparent availability of information to the public has been increasingly emphasized in many U.S. and international environmental or public health documents, including EPA's Mission Statement, the Rio Declaration on Environment and Development, the Aarhus Convention, and a recent review by the then head of CDC, Thomas Frieden, who in enumerating the public health actions of a responsive government, listed the first as "(p)romoting free and open information" (see Goldstein, 2016, for review). Major oil spills inherently are stressful to affected communities. Lack of transparency enhances the stress levels and psychosocial impact of any risk-related situation. As occurred during DWH, the choice of a dispersant that has a proprietary component contributes to this problem and also may limit the extent of toxicological information immediately available (Goldstein, 2010b). Lack of transparency also contributes to the "social amplification of risk," a phenomenon highly dependent on how much trust is accorded by individuals and communities to the information source (Kasperson et al., 1988; Slovic, 1987). Secrecy, whether justified or not, unfailingly decreases trust and the willingness of the public to follow recommendations or to be involved in the stakeholder engagement processes, which are central to risk communication (Walker, 2016; Walker et al., 2015). Loss of trust also increases the amount of time that decision makers must devote to responding to public concerns. Accordingly, the presence or absence of undisclosed, and potentially proprietary components in a dispersant formulation could be considered among the determinants in choosing a dispersant in response to an oil spill. This could be extended to include the cleaning agents used in decontamination activities during a spill.

Wherever possible, full disclosure of a confidential business information agent could accompany initial use. If the authorities are not willing to strongly reassure the concerned public in the midst of a disaster such as the DWH oil spill that a secret ingredient in a dispersant is harmless, it would be best not to use that dispersant.

After the DWH oil spill, CDC disseminated a useful document aimed at local health professionals: “Gulf Oil Spill 2010: Deep Water Horizon Human Health Interim Clinical Guidance.” The CDC document did not provide health guidance on dispersants, however. In order to facilitate early dissemination of guidance to local health professionals after the next oil spill, CDC could update its guidance document to include appropriate information about dispersants in the near future.

Integrating Human Health Considerations into Modeling Efforts

Ultimately, each one of the direct and indirect dispersant-related scenarios described above must be considered in a comparative risk context. For example, mechanical (booming and skimming) and controlled burning of surface oil are among the other techniques available to decision makers for responding to an oil spill. A reasonable question is how each of these alternative methods compares with dispersant use in terms of the potential for human health effects. For example, burning of a complex hydrocarbon mixture such as crude oil could lead to greater inhalational exposure to PAHs and benzene for the worker population. As discussed in the toxicological evidence section, the PAHs produced by combustion are somewhat different in chemical structure and in component mixture than are those naturally present in crude oil and likely have different toxicological properties. Air emissions after in situ burning have been characterized (e.g., Gullett et al., 2016; Ross et al., 1996; Schaum et al., 2010); however, it is difficult to estimate occupational exposure from these studies. There are also direct risks of fire that can and should be fully containable but are not zero.

Chapters 6 and 7 discuss more fully the current efforts to make comparisons across oil spill control techniques using integrated models. The integration of human health effects into these models are just beginning, and some interesting initial findings are worth noting. Gros et al. (2017) modeled the ascent of DWH oil from the seafloor to the surface and validated their model by comparing hydrocarbon concentrations at various levels in the water column to observations during the DWH response. They found that SSDI reduced VOC atmospheric concentrations by 28% overall, with a benzene estimated reduction of 2,000 times. These results assume a dispersant injection of 0.4%, the average for the DWH time period (Spaulding et al., 2017). Had a 1% injection been used, subsequent calculations by Socolofsky and Gros (see Appendix E) and described in Chapter 7 suggest a greater reduction in benzene concentration at the surface. Crowley et al. (2018) also suggest that SSDI can substantially reduce VOCs at the surface. Using model simulations of a deepwater blowout under varying conditions (described in further detail in Chapter 7), they evaluate how SSDI affects the spatiotemporal pattern of VOC concentrations in the atmosphere above the blowout. Simulations suggest that SSDI reduces VOC concentrations within a 2 km radius of the release site. This reduction in VOC levels around the wellhead would conceivably lead to better access and hence quicker response as well as reduced exposures for well-control responders, because responders often move out of areas when measured levels are a health concern. However, current oil spill fate models do not explicitly model dispersant components and do not include aerosols, which could be an important exposure route for both occupational and community exposure scenarios (Afshar-Mohajer et al., 2019). In addition, integrated models that include risk estimates from ingestion of seafood would also be useful.

Until analysis of the impact of dispersant use focuses not just on the hazard component of risk but also on the spill duration and number of people involved in the response, computing the value of shortening the response period by using dispersants as compared to other response approaches is not possible. Future work could consider whether or not dispersant use results in a shortened duration and subsequent alteration in occupational injury and illness risk related to tasks performed as well as seafood safety closure periods, when dispersants are used versus when they are not used.

FINDINGS AND RECOMMENDATIONS

Finding: Epidemiological studies examining the association between dispersant exposure and health outcomes after the *Deepwater Horizon* (DWH) oil spill have reported respiratory and dermal effects in responders; however, drawing conclusive results from these studies is hindered by limitations inherent to the DWH response. In particular, the protracted initiation of the studies and the lack of a dispersant/dispersed oil biomarker necessitated reliance on self-reporting, making it difficult to accurately estimate exposures and hence effects of dispersant/dispersed oil versus oil alone in response workers and the general community.

Recommendation: Selection of biomarkers to improve human exposure assessment should consider the toxicity of dispersant and oil components and degradation products (produced by both biological and photodegradation), persistence in the environment, and bioaccumulation potentials. Biomarkers and analytical protocols should be established for each dispersant formulation listed on the U.S. Environmental Protection Agency's National Contingency Plan Product Schedule.

Recommendation: In advance of the next significant oil spill, the reporting requirements for details of injury and illness reporting for worker health and safety should be improved, with a clear focus on whether workers were exposed to dispersant. To that end, publication and ready availability of well-defined DWH worker health and safety statistics is needed. Exposure assessment and toxicological evaluation should recognize that response workers may not be from a healthy worker population and may not know how to minimize exposure.

Recommendation: Consideration should be given for ongoing evaluation, alone and together, of the U.S. Coast Guard and the National Institute of Environmental Health Sciences cohorts, and lessons learned from the methodological limitations of the DWH studies should be applied to future studies of dispersant use. As some workers appear to have been included in both studies, the committee recommends that the two groups of investigators assess the extent to which their findings for these workers corroborate each other.

Recommendation: Approaches such as a Spill Impact Mitigation Assessment should be used to assess potential trade-offs associated with such a wide-ranging emergency response. If the use of dispersants might change the response time and duration of the response—and hence, person-hours worked—the potential impact on the injury hazard rate should be part of the risk-benefit decision analysis.

Finding: Tracking oil in the water column and sediment may be more informative for determining locations in which fisheries may be affected and for initiating fishery closures than observing oil at the surface. The protocol for reopening fisheries after DWH was criticized for not including testing for potential contamination from dispersants and for not accounting for the range of seafood consumption rates and meal preparation methods in local communities. There is inadequate information to determine whether dispersant use alters polycyclic aromatic hydrocarbon (PAH) uptake in fish or shellfish such that it would change the length of time before fisheries are reopened. Concentrations of dioctyl sodium sulfosuccinate (DOSS) measured in fish and shellfish tissue during and following DWH were low or nondetectable, suggesting negligible human health risk associated with dispersant exposure via ingestion of seafood.

Recommendation: During the pre-event planning phase, the National Response Team and Regional Response Teams should engage with the U.S. Food and Drug Administration, the National Oceanic and Atmospheric Administration, and state agencies with statutory authority for ensuring seafood safety to develop national, regional, and locally appropriate protocols that involve engagement of local communities for closing and reopening waters to fisheries. Such protocols should rely on direct measurement and projection of subsurface oil movement and potential for exposure (e.g., through integrated modeling). These protocols should also involve analytical methods to determine dispersant component concentrations within seafood. Furthermore, better understanding of whether dispersant use changes the length of time of fishery closures by altering PAH uptake could help in predicting its impact on community economic and psychosocial effects.

Finding: Large-scale oil spills result in mental and behavioral effects in community members. During the spill response following the DWH oil spill, the use of an unprecedented volume of chemical dispersant contributed to these effects. Furthermore, the publicity related to the lack of publicly available information on the chemical constituents of the dispersant formulations contributed to concerns.

Recommendation: Wherever possible, full disclosure of a confidential business information agent should accompany initial use. If the authorities are not willing to strongly reassure the concerned public in the midst of a disaster such as the DWH oil spill that a secret ingredient in a dispersant is harmless, it would be best not to use that dispersant. Furthermore, disclosure of real-time dispersant use information and up-to-date health risk information or guidance should be publicly available. Actively engaging public health authorities at the national and state levels early on to provide risk communications will improve transparency, and it may increase trust and understanding of health risks, assisting in mitigating the overall psychosocial impact of dispersant use during an oil spill.

CHAPTER 5

TOOLS FOR DECISION MAKING

INTRODUCTION

This chapter examines the response trade-off decision-making tools that were introduced briefly in Chapter 1. These decision-making tools are often used to compare and assess the benefits and drawbacks of various oil spill response options, and ultimately, they rely on an understanding of the fate of oil in the environment (see Chapter 2), the toxicity of dispersants and dispersed oil (see Chapter 3), and the potential human health consequences (see Chapter 4).

The response options considered for marine spills include surface and/or subsea dispersant, mechanical recovery, in situ burning, shoreline clean-up, protective booming, and natural attenuation. Often these response options are used in combination to effectively mount a comprehensive spill response.

"As the potential use of dispersants is expanded into nearshore, estuarine, and perhaps even freshwater systems, the trade-offs become even more complex" (NRC, 2005). While this is a true statement, the primary focus of dispersant use will continue to be for offshore oil spills in the marine environment where dilution can play a large part in mitigating potential negative effects. Although this chapter focuses on offshore marine environments, work has also been done on the use of dispersants in nearshore and coastal locations, and it is possible that there will be special cases where dispersant use could be valuable.

As discussed in Chapter 3, the toxicity of oil to marine organisms depends on the exposure of organisms to oil and the water-soluble compounds from the oil. The extent of toxicity depends on the exposure route, the concentration of the oil, and the duration of exposure. Water-soluble chemical compounds like aromatic hydrocarbons (components of crude oils) are typically more highly toxic to marine organisms (Di Toro et al., 2007) than are low-solubility compounds (e.g., most alkanes and cycloalkanes).

When dispersants are applied to treat floating oil, small oil droplets are dispersed into the upper water column. Surface oils will rapidly dilute if water depth allows (Bejarano et al., 2013). Marine organisms living within a few meters of the sea surface will therefore experience an increased exposure to oil (Singer et al., 1998), with the toxicity depending on the exposure duration (Bejarano et al., 2014b; Sterling et al., 2003). In the case of subsurface spills like a blowout or pipeline leak, dispersants may be injected at the seafloor. This will increase oil concentrations near the source but tend to decrease them further afield, especially at the surface. Marine organisms in the lower water column will be exposed to an initial increase of water-soluble oil compounds that will dilute in the water column over time (Lee et al., 2013a).

Dispersant application involves a trade-off between decreasing the risk to the surface and shoreline habitat and increasing the risk beneath the surface. The optimal trade-off must account for various factors, including the type of oil spilled, the spill volume, the weather and sea state, the water depth, the degree of turbulence, and the relative abundance and life stages of organisms (NRC, 2005).

Chemical dispersants may increase the risk of toxicity to subsurface organisms by increasing bioavailability of the oil. The reader is referred to Chapter 3 for a detailed discussion of oil and dispersed oil toxicity. However, it is important to note that at the 1:20 dispersant-to-oil ratio (DOR) recommended for use during response operations, the dispersants currently approved for use are far less acutely toxic than oil is. Toxicity of chemically dispersed oil is primarily due to the oil itself and its enhanced bioavailability (Lee et al., 2015).

As discussed, dispersants are considered a potential response tool in many countries. Different decision-making processes are used to determine whether to proceed with dispersant application, but, typically, a list of dispersants that may be applied is developed along with an approval process for their actual use. See Chapter 7 for further discussion.

DECISION-MAKING TOOLS

As previously discussed, making the best decision possible during an oil spill incident requires a balanced consideration of the potential environmental consequences of the spill under a natural recovery scenario versus the consequences associated with each response strategy. In any spill response, the first priority is the protection of human life, and the Federal On-Scene Coordinator and Area Contingency Plans place the highest priority on decisions that may affect response worker health and safety or public health (in the case of a nearshore release). Once immediate worker and public health and safety considerations are addressed, the next priority is to develop a response based on the best combination of response strategies that most effectively reduces environmental consequences, offers the greatest resource protection, or promotes faster recovery. However, determining the preferred response approach requires a time-sensitive evaluation of multiple factors (see Figure 5.1).

Critical to informing response decisions is the identification of resources that are at risk to adverse effects. Special consideration is given to resources within the area of potential effects that are of socioeconomic, ecological, cultural, or archaeological significance, and, in particular, to those resources that are protected under U.S. federal laws or comparable regulatory requirements around the world. In the United States, for example, these resources include species listed under the Endangered Species Act, designated Essential Fish Habitat under Section 305(b) of the Magnuson–Stevens Fishery Conservation and Management Act, and archaeological sites recognized under Section 106 of the National Historic Preservation Act.

For ecological resources, trade-off decisions were originally made based on such key factors as length of recovery from potential effects, but emphasis is shifting toward the use of ecosystem services: that is, the goods and services supplied to humans by natural resources (see the Ecosystem Services section at the end of this chapter). In the case of length of recovery, habitats or animals that are anticipated to experience slow recoveries to baseline conditions are generally given greater protection, and thus a greater weight in trade-off decisions. Recovery rates are resource-specific but are usually expected to be longer for resources that have slow growth rates, long life spans, and

FIGURE 5.1 The decision-making process for selecting the optimal response option requires a thorough understanding of overall response goals and priorities; that is, knowing what response options are available and feasible, where the oil is heading, and what resources will be potentially affected by the spill or spill response activities.

low reproductive output. With an emphasis placed on recovery, protection is generally assigned to entire populations rather than individuals, with the exception of protected species. In the case of ecosystem services, emphasis is placed both on the contributions of ecological systems to humans and on the results in response option selection that is guided by restoration of the most valuable resources.

In 2000, IPIECA (formerly the International Petroleum Industry Environmental Conservation Association) published a report titled *Choosing Spill Response Options to Minimize Damage: Net Environmental Benefit Analysis* (IPIECA, 2000). The report highlighted the importance of "close cooperation between industry and national administrations . . . to ensure the maximum degree of coordination and understanding." Furthermore, the report emphasized that when all involved parties work together, there is a greater likelihood of mitigating potential damages to the ecosystem.

This report was the original guiding document for using the Net Environmental Benefit Analysis (NEBA) concept for oil spill response decision making, and it has since been revised (IPIECA-IOGP, 2015). While the understanding of the science of dispersant use has evolved in the past decade, there are still gaps. Therefore, NEBA-based approaches should clearly identify information gaps that exist at the time the process has commenced.

In the past two decades, three decision-making tools have evolved to help implement the NEBA concept (see Box 5.1):

- Consensus Ecological Risk Assessment (CERA)
- Spill Impact Mitigation Assessment (SIMA)
- Comparative Risk Assessment (CRA)

These tools can bring together elements of various regulations, policies, and current state of the science into an overall decision-making framework for oil spill response. The tools are not limited to application in a particular regulatory regime or natural system (e.g., marine, estuarine, or freshwater environments), but they can be adapted to a wide range of scenarios.

BOX 5.1
Summary of the Trade-Off Decision Tools

Past Consensus Ecological Risk Assessments (CERAs) and Spill Impact Mitigation Assessments (SIMAs) have used modeling inputs from OILMAP, OSCAR, or GNOME/ADIOS 2 (depending on spill scenario), and both use a structured approach to seek consensus among stakeholders on effective response methods that produce the lowest environmental risk. There are differences between these tools and how they are best used in spill responses.

Consensus Ecological Risk Assessment

CERA utilizes a detailed semiquantitative risk ranking square to perform comparative analyses of available response methods. The risk squares assign two scores, one for extent of exposure and a second for duration of recovery. CERA originally did not consider socioeconomic or commercial factors, but it was modified in 2012 to add these factors and again in 2015 to add worker health and safety. A recent industry project in the Shelburne Basin of Eastern Canada utilized the CERA tool (Coelho et al., 2015), and the CERA method is also still actively used by the U.S. Coast Guard, the U.S. Environmental Protection Agency, and the National Oceanic and Atmospheric Administration (NOAA), including several recently conducted CERAs in Delaware Bay for light Bakken shale oil and diluted bitumen transportation (Walker et al., 2016) and in Hawaii (Walker et al., 2018b).

CERA is frequently used as a risk communication method that can add value by getting stakeholders together in workshops to reevaluate and update Area Contingency Plans and Oil Spill Response Plans. It is also a mechanism for building trust among stakeholders and resource trustees by exchanging ideas and perceptions during non-spill response conditions. One drawback of CERA is that it requires considerable time and planning to get participants to workshops. As a result, it is an appropriate tool at the **Contingency Planning Level** but holds limited value as a real-time decision tool during a response, as there is insufficient time to execute this level of detailed scientific literature review during a spill. The reader is referred to the NOAA Office of Response and Restoration website[a] for the latest information on CERA workshops.

Spill Impact Mitigation Assessment

SIMA utilizes a risk ranking process that uses a single score for extent of exposure and duration of recovery and then adds a weighting factor for resource values based on local priorities. Unlike CERA, the SIMA approach front-loads the process of obtaining stakeholder consensus on resource priorities when assigning the weighting factor via information retrieved from the Environmental Impact Statement or other biological assessments conducted during the permitting process. As such, SIMA can be done quite quickly and is therefore a useful tool for use by the Incident Command System Environmental Unit at a **Strategic Level** during the early hours of a spill response to document current priorities and response decisions. Another advantage of SIMA is that it can be very quickly reevaluated (rescored) on a near daily basis to support ongoing changes in spill conditions at the **Tactical Level.**

SIMAs have been conducted in North America and abroad since the tool was introduced in 2017 in support of permitting requirements, development of Oil Spill Response Plans, tabletop spill response exercises, and large-scale spill drills (Coelho et al., 2017a; Slaughter et al., 2017).

Comparative Risk Assessment

The CRA is the latest concept in response trade-off tools and is different from CERA/SIMA in that it includes both a trajectory *fate* model and an *effects* model. This adaptation provides an objective way to quantify the effects of the spill rather than relying on local stakeholders and experts to qualitatively score the effects. It also permits the user to weight certain resources above others (e.g., protected species). A CRA is scenario dependent and results will typically take many days of computer time to produce. Hence, it is a tool better suited to contingency planning than to tactical planning during an actual spill.

Spill response decision making cannot purely be simplified into “modeling and numbers”; it ultimately comes down to trying to satisfy a complex series of trade-offs and hopefully reaching consensus among the members of the Unified Area Command. Workshops involving stakeholders with access to fate and trajectory models are a key step to optimizing trade-offs and resolving inevitable conflicts and erroneous

BOX 5.1 Continued

preconceptions. For example, in a CERA workshop conducted in Alaska, an examination of the trajectory model output suggested that aerial dispersant would have reduced shoreline oiling. However, in this region, the local stakeholders believed that oiling the shoreline was a preferred option to putting oil into the water column, as it aligned with their value system and key subsistence biota. This level of understanding about local priorities requires tools and methods that can be flexible, and all three of these tools incorporate mechanisms for weighting importance of locally important species or habitats. In summary, all three decision-making tools have value and each can be used in uniquely different ways to evaluate dispersants at the Area Contingency Plan level, for strategic planning at spill onset by the Unified Area Command, or at the tactical level within Incident Command System Environmental Unit. The trade-off decision and communication processes continue to be studied and refined (Bostrom et al., 2015a,b; Leschine et al., 2015).

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[a] See https://response.restoration.noaa.gov/oil-and-chemical-spills/oil-spills/resources/ecological-risk-assessment-era-workshops.html.

Integrated models play an important role in each of these decision-making tools, as is explained later in this chapter. A basic representation of typical inputs to these decision-making tools is presented in Figure 5.2.

INTEGRATED MODELS

Several possibilities exist with respect to informing the oil spill response decision-making process as it pertains to possible and actual effects. One option to quantify dispersant trade-offs is to use laboratory or field experiments, although this approach faces steep challenges in replicating the complexity and individualist nature of a real spill. A second option may be to rely on experience from past spills, but these rarely include comprehensive, high-quality observations and, additionally, may be different from the spill being considered in important ways. Another option is to wait until the spill happens and monitor key indicators in the field during the event. This route has many potential pitfalls, one of the most important being the difficulty in getting sufficient monitoring equipment in the right place at the right time. Furthermore, real-time monitoring cannot itself forecast future effects and does not support the exploration of "what-if" scenarios. Given these limitations, integrated models are routinely used—especially in contingency planning—to quantify the trade-offs involved in dispersant usage.

As a tool to guide decision makers evaluating trade-offs, integrated models provide a number of advantages. Models incorporate many of the processes of importance and can provide a "big picture" view of the fates and effects of a spill in many different formats. From the perspective of "fates," integrated models have the ability to handle different oils, gas ratios, and flow rates as well as ocean and atmospheric conditions. Some models can factor in the removal or diversion of oil by skimmers, booming, burning, etc. From the perspective of "effects," a few of the models use their calculated 4-D (x, y, z, and t) concentration fields of oil pseudo-components coupled with toxicity thresholds and spatial distributions of important biota to calculate mortality and recovery rates. Another benefit of integrated models is that they can be used to quantify and understand the sensitivity of the results to changes and uncertainties in inputs and sub-model formulations and the effectiveness of the various response options. Sensitivity studies are especially helpful in establishing confidence limits and focusing future research on topics that will best improve our understand-

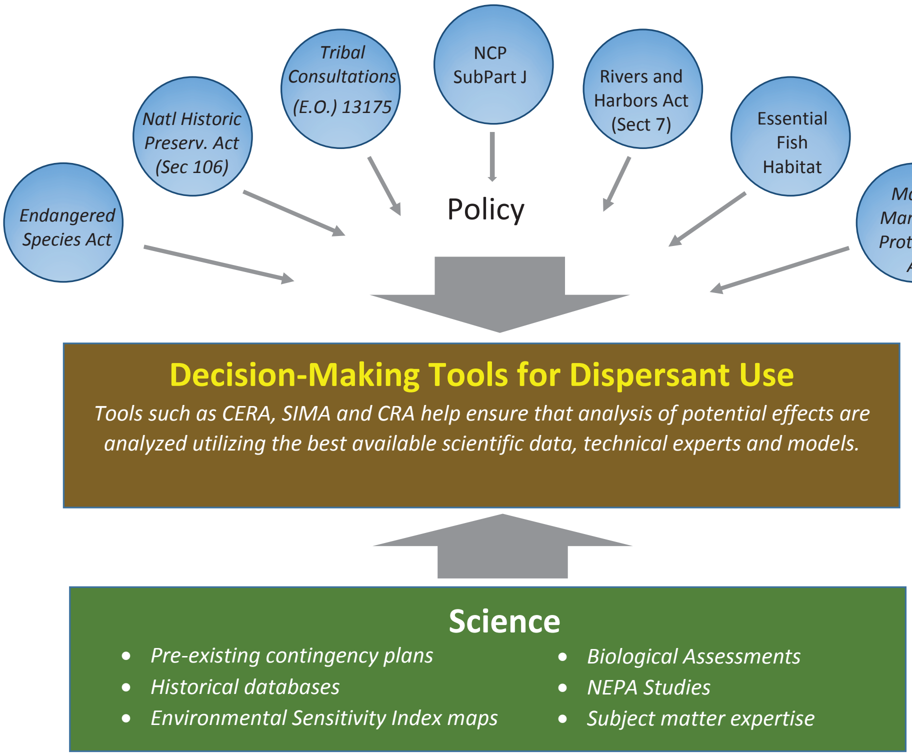


FIGURE 5.2 CERA, SIMA, and CRA bring together elements of regulations, policies, and current scientific information. This figure provides some examples for illustrative purposes. SOURCE: Modified from Coelho et al., 2017b.

ing of spill effects. Finally, a model can provide a forecast that reflects changes in weather, flow rate, and response alternatives.

As briefly mentioned, it is difficult to make trade-off decisions using field observations during an ongoing spill. The most important reason is that observations made during actual spills are almost always limited because the vast majority of efforts expended during a spill are focused on ensuring human safety, containing the oil (including source control), and minimizing the overall environmental damage. These activities will typically have priority over monitoring, and this often results in restrictions on scientists trying to gain access to key resources or critical locations (e.g., the wellhead in a blowout). Additionally, there are rarely opportunities during a real spill to conduct robust sensitivity studies. For example, during a blowout being treated with subsea dispersant injection (SSDI), it would be informative to turn SSDI on and off under comparable conditions to assess its effectiveness. However, on-scene responders, as well as other stakeholders, may be unwilling to interrupt this response option if they believe it is reducing volatile organic compounds to safer levels. There were periods during the *Deepwater Horizon* (DWH) oil spill when SSDI was reduced substantially for operational reasons; determining the effect of this action was difficult to assess, however, because the interruptions were too short, the observations too sparse, and the environment too dynamic.

Similarly, using results from lab experiments to guide trade-off decisions poses some limitations. First and foremost is the issue of complexity. The natural world contains countless processes that are difficult to simulate in a lab setting, effectively limiting the applicability of laboratory results to predict real-world outcomes. Another issue with relying solely on experimental results is the notion of "scale." Even the largest lab facilities are typically orders of magnitude smaller than the environment in which an actual oil spill occurs. This constraint bounds the comprehensiveness of experimental testing, which has implications in the universality and accuracy of the models that are based on them. This is especially important in the study of such critical processes as deep ocean oil and gas droplet formation and evolution as oil travels from the subsurface, high-pressure environment to the surface.

Large-scale field studies, such as DeepSpill (Johansen et al., 2003), have provided important information regarding the behavior of gas and oil released at depth. Like all studies, however, its scope was limited, and in the case of this experiment, it did not include an oil spill treatment process such as SSDI. It is unlikely that a future deep-sea oil release field experiment involving SSDI would be permitted to allow shoreline oiling, although such a study design would provide valuable insights on the fate and effects of untreated oil versus subsea dispersed oil in this environment. If such a comprehensive study was successfully executed, the results would be best used to improve models rather than to expect that the experimental results could be directly applied to the next spill.

Integrated models also have limitations. Some of the complex processes resident in the environment are poorly understood and their interactions may be even less so. Mathematically describing the behavior of oil in the environment through an integrated model and subsequently validating its results is difficult largely as a result of the lack of definitive observations taken during historical spills. On a positive note, however, integrated models are composed of sub-models simulating the major processes, and these sub-models have typically been validated. Nevertheless, results from even the best integrated model should be viewed with caution and results with uncertainty bounds should always be presented to decision makers, a point reinforced by ASTM F2067-13 (ASTM, 2013b). Unfortunately, the American Society for Testing and Materials does not provide guidelines on how to construct such bounds, which is not surprising given the complexity and lack of research in this topic with regard to integrated models.

Errors and uncertainty in modeling stem from two general sources commonly referred to as aleatory and epistemic. Aleatory uncertainty originates from variability in key model inputs such as wind or current forcing, oil flow rate, etc. Quantifying some forms of aleatory uncertainty is fairly straightforward when historical observations are available and the model is run in a "hindcast" mode, an approach that is commonly used in strategic (contingency) planning by using Monte Carlo simulations. Aleatory uncertainty due to wind could be included in tactical (real-time) forecasts by utilizing the standard ensemble wind model forecast products, but this would require running the model 30 or more times. To the committee's knowledge this has not been done.

Epistemic error arises from uncertainty in our understanding of the underlying physical, chemical, biological, etc., processes. Epistemic error is generally less well studied and more difficult to quantify than is aleatory error. Ideally, an integrated model could estimate the epistemic error by changing sub-model formulations, or at least by running sensitivity studies to understand the impact of uncertainty in the various sub-models on key model outputs. Similarly, an integrated modeler would ideally perform sensitivity studies to understand how changes in key model inputs (aleatory errors) affect important model metrics. French-McCay et al. (2018b) has recently studied the impact of droplet size on fates, and this work shows that uncertainty in droplet size models can have a substantial impact on calculated effects. In other words, the uncertainty in calculated fates coming from the uncertainty in just one sub-model (droplet size) can be substantial and could potentially alter the decision to use SSDI in a blowout.

Finally, it should be pointed out that integrated models often provide poor forecasts when used in an actual spill, particularly as the forecast time horizon increases (e.g., a forecast at 2 days will generally have a smaller error than a forecast at 1 week). It is not uncommon to see integrated models asked to provide a tactical forecast many days in advance even though the confidence bounds in the underlying weather and current forecasts are huge. A closer look at failed forecasts often reveals that there is nothing wrong with the integrated model; rather, the problem is with the input of winds and/or currents, which are generally derived from numerical models. As a case in point, Cooper et al. (2016) looked at operational current forecasts in the deepwater Gulf of Mexico based on state-of-the-art real-time measurements and models and found weak correlations: that is, r^2 values of only about 0.4 were obtained for a 2-day forecast horizon. Notably, a numerical model outperformed two seasoned experts. On the other hand, this same current model can provide very accurate hindcasts. As a result of this, it may be said with some confidence that the uncertainty bounds on integrated model results for strategic (contingency) planning will be much smaller than the bounds for tactical forecasts for most sites around the world. In other words, the inability of an integrated model to accurately forecast spill fates days in advance during an actual spill should not be taken as proof that the model cannot be trusted to develop a reasonable contingency plan.

Even if the uncertainty in integrated models was thoroughly studied and quantified, there would still be a major challenge: ensuring that decision makers take adequate account of this added information. The reality is that most major decisions in actual spills are not done with quantitative methods that could explicitly account for uncertainty statistics. Instead, decisions are usually made by professional judgment with some attention paid to average (expected value) model results.

In summary, optimizing the strategic (planning stage) and tactical (real-time) response to an oil spill scenario requires an understanding of the trade-offs of the response alternatives. It is doubtful that optimal decisions can be based solely on the existing observational database or previous experience. Thus, a well-validated and well-understood integrated model run by a knowledgeable operator can be an essential tool for the decision maker looking to choose an appropriate response strategy. The model results will have substantial uncertainty and it is desirable to quantify those, but the present state of doing so is rudimentary at best, and effective communication of uncertainty remains a challenge in providing information for decision makers (Bostrom et al., 2015a). It is essential for end users of these models (e.g., spill response decision makers) to understand the limitations and errors within these models when using this type of tool to select incident-specific response options.

The next section defines what we consider to be an integrated model. Some of the more commonly used integrated models are summarized with a discussion of their origin, scope, previous real-world applications, and validation. Two of those models will be used in Chapter 6 to evaluate the trade-offs involved in dispersant use.

Overview and Comparison of Integrated Models

Figure 5.3 shows the major modules that would be involved in a complete oil spill modeling system, which includes the four modules in the yellow ovals:

1. **Blowout module (where appropriate),** which would, at a minimum, calculate the droplet size distribution and simulate the buoyant plume. It could consider formation of hydrates and dirty (see Chapter 2) bubbles. The blowout module would be bypassed in the case of a surface oil release. Output from the blowout module would consist of 4-D snapshots of hydrocarbon pseudo-component concentrations that feed into the physical fate module.
2. **Physical fate module,** which would track the hydrocarbons until they reach their ultimate fate. It would include such physical transformations as surface spreading, dispersion, advection, and entrainment. It would also include such weathering processes as dissolution, evaporation, photooxidation, biodegradation, etc. The ultimate product of a fates module is 4-D snapshots of concentrations of the hydrocarbon pseudo-components in the ocean.

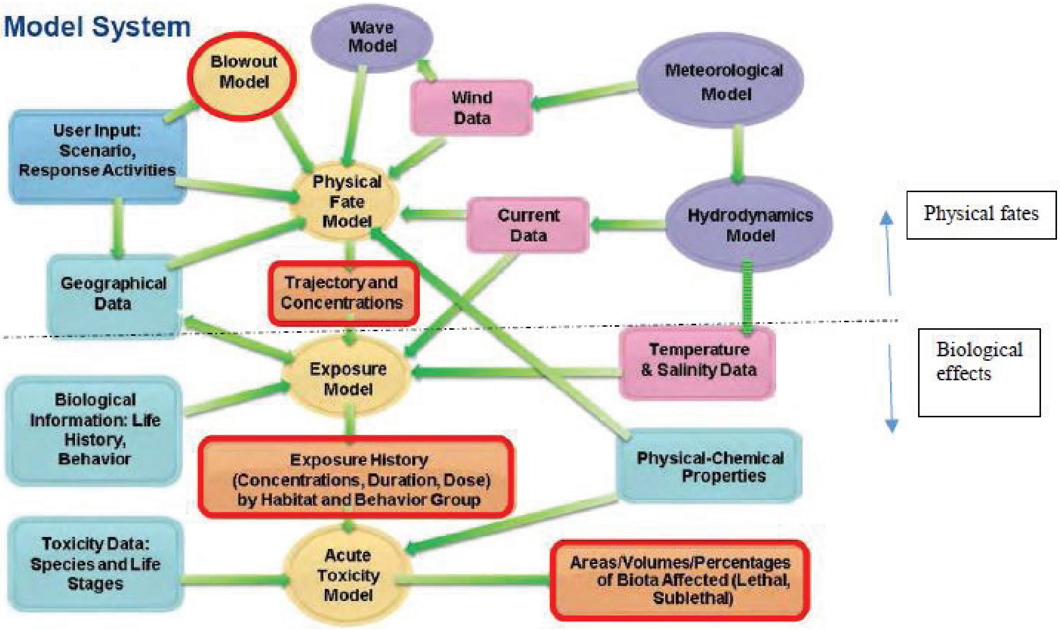


FIGURE 5.3 Schematic showing the major components of an integrated oil spill model for the ocean. Tan blocks show the major modules of a complete integrated model. The blowout module would be bypassed in the case of a surface oil release. Blue, purple, and magenta blocks show the major external databases or models that must be provided to the integrated model. The orange blocks indicate major deliverables from the modeling. SOURCE: Modified from French-McCay, 2017.

3. **Exposure module,** which calculates the exposure duration of important biota to the 4-D concentration fields.
4. **Toxicity module,** which estimates the acute and chronic effects on the biota based on thresholds, toxic units, or some other metric.

Integrated models require considerable input data; these are indicated by the compartments colored blue, purple, and magenta in Figure 5.3. The primary products from the modules of the integrated model are shown in orange.

Table 5.1 summarizes several of the more widely used integrated models as well as the Texas A&M Oilspill Calculator (TAMOC) model. Part A of the table covers fates while part B covers effects. Each row describes a major process while each cell briefly describes the methodology. In the case of fates, many of these are fairly standard sub-models so the methodology description is limited to a few key words. Standard, well-documented sub-models are not as typical for effects; hence, these are described in greater detail.

Table 5.1 is intended as a summary of the models and does not capture many subtleties and may leave out some capabilities. Because a comprehensive review of all oil spill models is outside the scope of this report, the interested reader is referred to Bejarano et al. (2013) for a high-level overview of several other models or to the references in the second row of the table.

SIMAP/OILMAP and OSCAR are commercial models that have been used to estimate both fates and effects. The NOAA GNOME/ADIOS2 model is the most comprehensive publicly avail-

TABLE 5.1A Summary of Fates Incorporated in Several Representative Integrated Models

Sub-model	RPS ASA SIMAP/OILMAP DEEP	SINTEF OSCAR/DREAM	NOAA GNOME/ADIOS2	TAMOC
Overall model	French-McCay (2003); French-McCay et al. (2018a); Spaulding et al. (2017)	Reed and Hetland (2002)	Barker et al. (2018)	Dissanayake et al. (2015); Gros et al. (2017); Socolofsky et al. (2015)
Droplet model	Equilibrium model, Li et al. (2017)	Equilibrium model, Johansen et al. (2013)	Specified by user; have used Johansen et al. (2013)	VDROP-J, Zhao et al. (2014a)
Plume model	Integral plume, Spaulding et al. (2017)	Integral plume, Johansen (2000)	TAMOC, Socolofsky et al. (2015)	Integral plume, Dissanayake et al. (2018)
Hydrates	Not included	Johansen et al. (2000)	TAMOC, Socolofsky et al. (2015)	Dissanayake et al. (2015); Socolofsky et al. (2015)
Dissolution	Raoult’s Law, French-McCay et al. (2015)	Reed et al. (2001)	Stevens et al. (2015); Thibodeaux and Overton (2014)	Real-fluid fugacity and modified Henry’s Law, Gros et al. (2016, 2017)
Biodegradation	1st order decay, French-McCay et al. (2015); Spaulding et al. (2017)	1st order decay, Brakstad and Faksness (2000)	1st order decay with droplet size dependence, Thrift-Viveros et al. (2015)	1st order decay but not used in Gros et al. (2017)
Evaporation	Raoult’s Law, French-McCay et al. (2015)	Raoult’s Law, MacKay et al. (1980)	Jones (1997)	Raoult’s Law, Drozd et al. (2015), and Gros et al. (2017)
Photooxidation	1st order half-life based on seasonal mean UV in water column, French-McCay et al. (2018a)	Included through usage of weathering data of oils exposed to sunlight.	None	None
Entrainment	Adaptation of Delvigne and Sweeney (1988) with updated droplet size model. Li et al. (2016, 2017b)	Mass flux: Delvigne and Sweeney (1988); Droplets: Johansen et al. (2015)	Update of Delvigne and Sweeney (1988), see Barker et al. (2018)	None
Particle interaction and deposition	Interaction rate based on particle concentration. French-McCay (2004); French-McCay et al. (2015)	Dissolved particles can interact with nepheloid layer and transfer to the sediment: Reed et al. (1995)	Payne et al. (1987)	None
Advection	3.5% of wind + background current, French-McCay (2004)	3.5% of wind + background	User specified windage factor + background current added using 2nd order Runge-Kutta, Barker et al. (2018)	None

Spreading	French-McCay (2004); Hoult (1972)	Fannelop and Waldman (1972)	Initial: Fay-Hoult, then Richardson-scaled turbulence, with Langmuir correction, Barker et al. (2018)	None
Emulsification	French-McCay (2004); MacKay and Zagorski (1982)	Daling et al. (1990)	MacKay and Zagorski model (1982) or Lehr (2017)	None
Dispersion Horizontal	Randomized (Bear and Verruijt, 1987) dispersive velocity which are scaled using Okubo (1971). Scaling can be a function of vertical layer.	Random walk, Okubo (1974); Reed and Hetland (2002); Reed et al. (1995)	Random walk, Barker et al. (2018)	None
Dispersion Vertical	Randomized (Bear and Verruijt, 1987) dispersive velocity which are scaled using Okubo (1971). Scaling is a function of vertical layer.	Ichiye (1967)	Random walk in two zones: Mixed layer and sub-mixed layer, Barker et al. (2018)	None
Droplet rise (above plume)	Modified Stoke's Law, White (2005)	Johansen (2000)	Modified Stoke's Law, White (2005)	Empirical equations from Clift et al. (1978)
Response	Skimmers, burning, surface dispersant, SSDI, French-McCay (2004); French-McCay et al. (2018a)	Skimmers, surface dispersant, SSDI, Reed et al. (1999)	Skimming, burning, dispersants, Barker et al. (2018)	None

TABLE 5.1B Summary of Effects Incorporated in Several Representative Integrated Models

Sub-model	RPS ASA SIMAP	OSCAR/ERA Acute
Exposure	Concentrations of whole oil and its components, as well as temperature, experienced by biota over time and space are tracked using Lagrangian elements assigned to behavior classes that move or remain stationary within habitats occupied by the organism types represented. Exposure is summarized as water volume or area where concentrations exceed ecological risk thresholds. In more detailed studies, the exposure history is evaluated to assess toxicity. (French-McCay, 2003, 2009, 2011, 2016)	Total hydrocarbon concentration (THC) is considered over four environmental compartments: surface, water column, seafloor, and shoreline. These are discretized in the horizontal domain on a grid of uniform size. Libre et al. (2018) used squares of 10 km.
Toxicity	Aquatic toxicity—A Toxic Units approach is used to account for the additive effects of the soluble and semi-soluble hydrocarbons dissolved from oil. LC50s for each hydrocarbon are estimated using the critical (lethal) body burden approach based on the toxicity model for narcotic effects. Mortality is a function of duration of exposure, i.e., the longer the duration of exposure, the lower the effects concentration (i.e., LC50). (French et al., 1996; French-McCay, 2002, 2009) Sediment toxicity—The equilibrium partitioning model is used to calculate dissolved concentrations of hydrocarbons in pore water from sedimented oil. The aquatic toxicity model is applied to pore water concentration estimates. (French-McCay, 2003, 2004, 2009; French et al., 1996) Wildlife—A portion of the wildlife in the area swept by oil slick over a threshold thickness is assumed to die, based on probability of encounter with the slick (based on behavior and habitats occupied) multiplied by the probability of mortality once oiled (based on dose-response data). (French-McCay, 2009, 2016) Habitats—Area of each habitat type exposed to oil over threshold thickness for effects (based on literature studies of effects thresholds).	General strategy: Impact = P[exposure] × P[lethality] × Population Frac. Surface water—Considers only physical contact with oil with the fraction of the valued ecosystem component (VEC) suffering mortality being a function of the fraction of the total surface covered by the VEC, the exposure time of the VEC to oil thicker than a threshold (2 μm for birds, 10 μm for marine mammals), the probability of encountering an area with surface oil, and the probability of lethal effects given oil encounter. The two later quantities are based on previous studies. Shoreline—Considers the National Oceanic and Atmospheric Administration's Environmental Sensitivity Index along with the average thickness of the oil, a patchiness factor, tidal range, length of shoreline, and slope of shoreline. Impact thresholds used in Libre et al. (2018) are 1 mm for vegetation and 0.1 mm for invertebrates living in the intertidal zone. Water column—Only considers egg and larvae. Calculates lethality using total hydrocarbon concentration and a species sensitivity distribution (SSD) curve parameterized using a LC5 of 58 ppb. Seafloor—For biota residing on the seafloor, lethality is calculated just as in the water column (see previous description). For biota residing in the sediment, concentration of THC in sediment is calculated through partitioning coefficient theory with lethality inferred from SSD curve.
Biomass density	Biomass density—Biological densities by life stage are developed based on sampling results, stock assessments, and life history information related to behavior and distribution. The densities are multiplied by volume or area affected to estimate numbers or biomass killed or otherwise affected. (French-McCay, 2003, 2004, 2009, 2011)	Biomass density—The density of valued ecosystem components are established in each vertical compartment and each grid using a monthly average.
Population level effects	Population models are used to estimate the number of years each species and life stage would have lived otherwise if not killed by the spill. Production foregone is estimate for fish and invertebrate species where growth models are developed. (French-McCay, 2003, 2009)	None

Biota recovery	For wildlife, fish, and invertebrate populations, recovery is typically assumed to occur once the individuals killed by the spill would have died anyway. For species where density-dependent population models are developed, recovery time is modeled as time until the population recovers to within 1% of the pre-spill condition. For habitats, recovery time is based on literature observations of productivity over time. (French-McCay, 2003, 2009)	Surface—Lag time for species breeding on shoreline depends on fraction breeding in contaminated sites. Restitution time depends on population loss and a discrete logistic growth model using a species-specific reproductive rate. Shoreline—Lag time based on three shoreline types. Restitution time is based on historical data for each Environmental Sensitivity Index where lethality has been exceeded. Water column—Restitution time considers critical threshold of fish population, above which recruitment is considered independent of spawning stock size. Also considers large mortality of larvae normally found in non-oiled environment. Sea floor—Lag time set to 1 year. Considers rate of decrease of THC, which is a function of bottom type.
Ecosystem-wide effects	Lost production (growth) of lower trophic level plants and animals (not explicitly modeled as individual species) is integrated in space and over time. Losses at higher trophic levels are estimated using a food web model and trophic transfer efficiencies.	None

NOTE: GNOME/ADIOS2 and TAMOC models do not contain effects sub-models and are therefore excluded from this table.

able model. Historically, GNOME has been used by NOAA, other government agencies, and private companies to serve as the core model for CERAs and SIMAs for surface oil spill releases. GNOME does include levels of concern derived from consensus ERAs and tracks over space and time whole oil concentrations on which to make assessments of potential effects (Mearns et al., 2001, 2003).

The TAMOC model focuses on the fate of oil from a subsurface blowout to the sea surface covering module 1 and part of module 2 of the four modules listed earlier in this section. However, these modules may be the most critical in determining the fate of oil from a blowout. While TAMOC is more narrowly focused than SIMAP/OILMAP, it uses more advanced algorithms for these processes. A closer look at Table 5.1A shows that none of the models directly include the coast, seafloor, or atmosphere. A truly complete integrated model of all oil fates and effects would incorporate these spatial regions.

TAMOC represents an important class of models that can be used in conjunction with the more comprehensive models like SIMAP/OILMAP. The latter models are time consuming to run, which inhibits their use as a tool in sensitivity studies or in studying new scenarios. Alternatively, models like TAMOC can be more readily run for different water depths, oil types, DORs, etc. Thus, one way to look at a new scenario (e.g., different water depth, distance from shore, oil type, gas-to-oil ratio [GOR], etc.) is to run the TAMOC model for the new scenario and then view the results from the perspective of SIMAP/OILMAP.

Socolofsky et al. (2015) compared 5 integrated models for 14 scenarios of a continuous 20,000 barrels (bbl) per day blowout. The models included SIMAP, OSCAR, and a predecessor of TAMOC. The scenarios considered two water depths (500 and 2,000 m), two GORs (500 and 2,000 std ft^3/bbl), two DORs (0 and 2%), and two horizontal current regimes (5 and 30 cm/s). Because of the importance of droplet size, all the modelers used the same droplet distribution for several of the cases. In several other cases, the modelers used their preferred droplet model. Models were compared by looking at four metrics, the most important being the mass of oil entering the intrusion layer and the downstream distance to the center of surfacing oil. Important conclusions were:

1. There is a consensus of the models that the addition of subsea dispersant moves the surfacing oil downstream by an order of magnitude and results in far less oil reaching the surface.
2. For a dispersed oil, a decrease in droplet size of ~25% can increase the volume of oil in the intrusion layer by a similar amount, but it causes much larger changes in the downstream surfacing distance (five times). This suggests that the present uncertainty in droplet models (up to two times, as described in Chapter 2) will affect the assessment of SSDI effectiveness substantially.

There are considerable discrepancies between the models for many of the metrics, and some critics of models have used this to question the credibility of all models. While the individual models have varying histories of development and validation, the two most validated and widely used (OSCAR and OILMAP Deep) produce fairly consistent metrics when they use the same droplet sizes. For example, Figure 11 of Socolofsky et al. (2015) shows that the distance from the release point to the downstream center of the surfacing oil compares to within two times for the majority of cases where a common droplet size was used.

THE CERA APPROACH

The integration of the NEBA concept into oil spill response planning in the United States increased in the mid-1990s when the U.S. Coast Guard (USCG) developed an approach to evaluate the ecological effects from various response options, which included input from several state and federal agencies. The effort was spurred by an article on the application of ecological risk analysis in dispersant use (Aurand, 1995), which outlined the essential elements of CERA. The USCG document, titled *Developing Consensus Ecological Risk Assessments: Environmental Protection in Oil Spill Response Planning: A Guidebook*, was later published in 2000, after a 4-year interagency development period (Aurand et al., 2000).

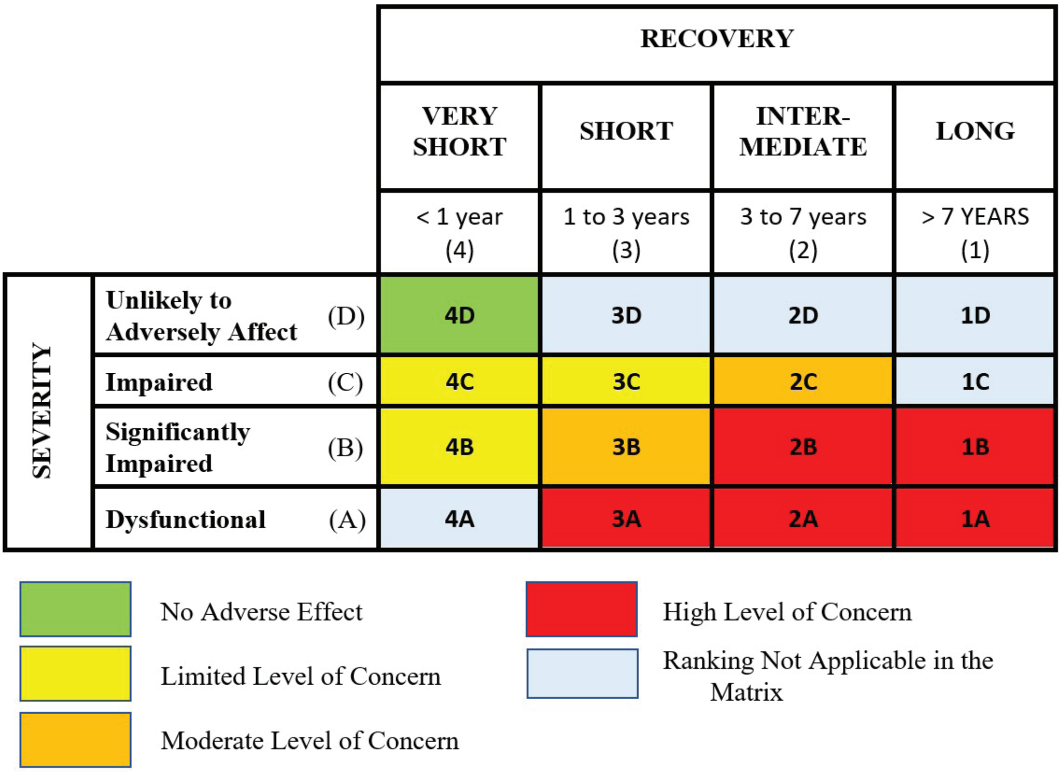
While this USCG CERA approach is nearly two decades old, its recommendation for using a blend of both common sense and consensus development as well as quantifiable scientific information remains a valid framework for response selection and continues to be used by industry and agencies. A detailed discussion of the CERA process was presented in the last National Research Council (NRC) dispersant report (see NRC, 2005, pp. 35-45).

The CERA process comprises three main phases: (I) problem formulation, (II) analysis, and (III) risk characterization, and it is intended to be conducted in a workshop setting that involves members of industry, operational response experts, response decision makers, scientists, and local resource experts. CERA participation has typically involved between 25 to 50 workshop participants but has varied. In Phase I, problem formulation, participants formulate a scenario for analysis, determine the relevant resources of concern and associated assessment thresholds, and they develop a conceptual model that directs subsequent analysis. In Phase II, analysis, the participants evaluate exposure, ecological effects, and recovery by customizing standard templates and simple analytical tools, like the risk square and a risk ranking matrix, for the specific spill scenario under consideration.

The risk square (see Figure 5.4) was incorporated in the CERA process because of its common use in other types of environmental assessments by the U.S. Environmental Protection Agency (MMS, 1989). It is a means to examine environmental risk by considering both the percent of a resource that is affected by a perturbation (in this case, an oil spill) and the anticipated time of recovery for a given resource. In the CERA method, a 4×4 matrix is frequently used, but during a given CERA workshop, participants customize this risk matrix by adding more columns or rows to provide greater resolution on either axis. Additionally, the length of recovery can be defined during the CERA process for a given scenario, depending on the anticipated recovery time for local resources. In one CERA (Aurand and Coelho, 2003), the slowest recovery period was defined as "> 25 years" due to coral structures in the region that, if harmed, could take a substantial amount of time to recover. Once the size of the matrix is set and the increments on each axis are customized for a given CERA, participants then color-code the risk square to qualitatively assign levels of concern. The flexibility in the CERA process allows participants to modify levels of concern, based on local expert input and stakeholder engagement, for the spill scenario under consideration. This aids the evaluation process of response option comparison later in the analysis.

The customization of templates during the analytical phase is an important step in developing consensus among CERA participants and helps ensure a common understanding of which resources are considered "important" in the local area and of how each response option will be appropriately deployed. During the workshops, the participants then use the risk square to evaluate the resource subcategories for each response option by assessing what percentage of each resource will likely be impacted and how long its recovery will take.

In Phase III, risk characterization, participants compare the overall environmental risks and benefits of each response option to those associated with natural recovery (i.e., baseline). The completed risk ranking matrix (see Figure 5.5) is the key to the CERA analysis as it enables compari-



		RECOVERY			
		VERY SHORT	SHORT	INTER-MEDIATE	LONG
		< 1 year (4)	1 to 3 years (3)	3 to 7 years (2)	> 7 YEARS (1)
SEVERITY	**Unlikely to Adversely Affect** (D)	4D	3D	2D	1D
	Impaired (C)	4C	3C	2C	1C
	Significantly Impaired (B)	4B	3B	2B	1B
	Dysfunctional (A)	4A	3A	2A	1A

🟩 No Adverse Effect

🟨 Limited Level of Concern

🟧 Moderate Level of Concern

🟥 High Level of Concern

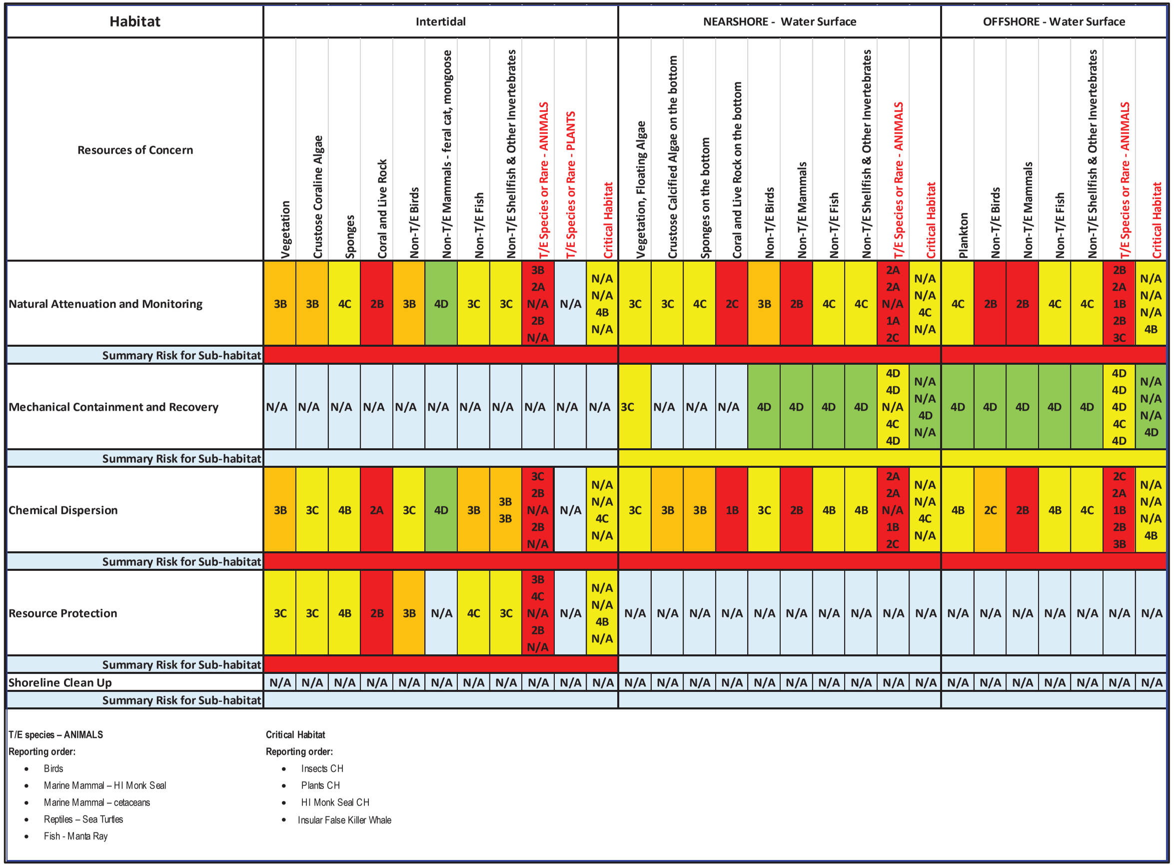
🟦 Ranking Not Applicable in the Matrix

FIGURE 5.4 A typical risk square used for a recent CERA (Walker et al., 2018b). This example shows a 4×4 matrix, but the CERA method encourages participants to modify the risk square by adding columns or rows, as needed, for a specific spill scenario under consideration. The participants can also customize the increments on either axis to account for local anticipated resource recovery times, based on inputs from local resource experts. In some CERAs, the recovery period on the "SLOW" end has been > 25 years. The final step of preparing the risk square is to have participants color-code the risk square to qualitatively assign no adverse effect (green), limited (yellow), moderate (orange), or high (red) levels of concern. This risk square is then used in the next step of the CERA process to assign a severity affected (A through D) as well as a recovery time (1 through 4) to every resource category for the anticipated risk for each response option. SOURCE: Walker et al., 2018b.

sons between response options and within particular habitats or resource groups. Figure 5.5 depicts conceptually how various resources of concern might respond when exposed to a response option. This figure depicts decisions from a recent CERA conducted in Hawaii, where CERA discussions were focused on potential surface dispersant application and relied on GNOME for oil trajectory and oil budgets (Walker et al., 2018b).

In the CERA, it is recognized that, in addition to the stress caused by the spilled oil, each response option may also be a source of ecosystem stress. The mechanisms that cause the stress vary as can the magnitude of stress resulting from each option. Seven "hazards" have been identified and represent the potential exposure pathways that connect the stressors (including natural attenuation) to the resources of concern. In summary, the hazards include:

"1. Air pollution;
2. Aquatic toxicity;
3. Physical trauma (i.e., mechanical impact from people, boats, etc.);



Habitat	Intertidal										
Resources of Concern	Vegetation	Crustose Coraline Algae	Sponges	Coral and Live Rock	Non-T/E Birds	Non-T/E Mammals - feral cat, mongoose	Non-T/E Fish	Non-T/E Shellfish & Other Invertebrates	T/E Species or Rare - ANIMALS	T/E Species or Rare - PLANTS	Critical Habitat
Natural Attenuation and Monitoring	3B	3B	4C	2B	3B	4D	3C	3C	3B 2A N/A 2B N/A	N/A	N/A N/A 4B N/A
Summary Risk for Sub-habitat	🟥										
Mechanical Containment and Recovery	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Summary Risk for Sub-habitat	🟦										
Chemical Dispersion	3B	3C	4B	2A	3C	4D	3B	3B 3B	3C 2B N/A 2B N/A	N/A	N/A N/A 4C N/A
Summary Risk for Sub-habitat	🟥										
Resource Protection	3C	3C	4B	2B	3B	N/A	4C	3C	3B 4C N/A 2B N/A	N/A	N/A N/A 4B N/A
Summary Risk for Sub-habitat	🟥										
Shoreline Clean Up	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Summary Risk for Sub-habitat	🟦										

Habitat	NEARSHORE - Water Surface									
Resources of Concern	Vegetation, Floating Algae	Crustose Calcified Algae on the bottom	Sponges on the bottom	Coral and Live Rock on the bottom	Non-T/E Birds	Non-T/E Mammals	Non-T/E Fish	Non-T/E Shellfish & Other Invertebrates	T/E Species or Rare - ANIMALS	Critical Habitat
Natural Attenuation and Monitoring	3C	3C	4C	2C	3B	2B	4C	4C	2A 2A N/A 1A 2C	N/A N/A 4C N/A
Summary Risk for Sub-habitat	🟥									
Mechanical Containment and Recovery	3C	N/A	N/A	N/A	4D	4D	4D	4D	4D 4D N/A 4C 4D	N/A N/A 4D N/A
Summary Risk for Sub-habitat	🟨									
Chemical Dispersion	3C	3B	3B	1B	3C	2B	4B	4B	2A 2A N/A 1B 2C	N/A N/A 4C N/A
Summary Risk for Sub-habitat	🟥									
Resource Protection	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Summary Risk for Sub-habitat	🟦									
Shoreline Clean Up	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Summary Risk for Sub-habitat	🟦									

Habitat	OFFSHORE - Water Surface						
Resources of Concern	Plankton	Non-T/E Birds	Non-T/E Mammals	Non-T/E Fish	Non-T/E Shellfish & Other Invertebrates	T/E Species or Rare - ANIMALS	Critical Habitat
Natural Attenuation and Monitoring	4C	2B	2B	4C	4C	2B 2A 1B 2B 3C	N/A N/A N/A 4B
Summary Risk for Sub-habitat	🟥						
Mechanical Containment and Recovery	4D	4D	4D	4D	4D	4D 4D 4D 4C 4D	N/A N/A N/A 4D
Summary Risk for Sub-habitat	🟨						
Chemical Dispersion	4B	2C	2B	4B	4C	2C 2A 1B 2B 3B	N/A N/A N/A 4B
Summary Risk for Sub-habitat	🟥						
Resource Protection	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Summary Risk for Sub-habitat	🟦						
Shoreline Clean Up	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Summary Risk for Sub-habitat	🟦						

T/E species – ANIMALS

Reporting order:

- Birds
- Marine Mammal – HI Monk Seal
- Marine Mammal – cetaceans
- Reptiles – Sea Turtles
- Fish - Manta Ray

Critical Habitat

Reporting order:

- Insects CH
- Plants CH
- HI Monk Seal CH
- Insular False Killer Whale

FIGURE 5.5 Example of a risk ranking matrix specific for resources inhabiting surface waters (0-2 m depth) in Hawaii, including threatened and endangered species, potentially affected by response options. For this CERA nearshore and offshore surface waters are defined as being within < 1 mi and > 1 mi from shore, respectively. The completed CERA delivers a final summary of results which color codes each option as no adverse effect (green), and limited (yellow), moderate (orange), or high (red) level of concern. The latter does not mean to stop actions, but rather to consult with resource managers on how to minimize impacts to the resources. Not applicable (blue) is also denoted. SOURCE: Walker et al., 2018b.

4. Oiling or smothering;
5. Thermal (i.e., heat exposure from ISB);
6. Oil-contaminated waste materials transfer and disposal; and
7. Indirect (refers to a secondary effect such as ingestion of contaminated food)" (Coelho et al., 2015).

The CERA process uses natural attenuation (also referred to as the no response option) as the baseline for the analysis. In addition, CERA assesses "levels of concern" on resource categories, habitats, and population assemblages, not on impacts to individual species. However, some protected species may drive a decision regarding how to best protect a given resource or habitat. The USCG guidelines (Aurand et al., 2000) provide a more detailed discussion of the CERA method, and the individual steps involved in conducting a CERA. A simple depiction is provided in Figure 5.6. Dozens of CERAs have been conducted for contingency planning purposes, and case studies are presented in the next chapter. Recent CERAs have been adapted to include socioeconomic and human health factors (e.g., Walker et al., 2016).

THE SIMA APPROACH

After the DWH oil spill there was a renewed effort to further refine the process of spill response decision making that could be applied globally in both industrialized and remote areas. Although the USCG had already developed the CERA process for contingency planning purposes, many believed that it could not be realistically applied at the onset of a spill response, nor tactically during an ongoing event. Simply put, the time, cost, and logistics coordination to achieve a consensus-based approach for contingency planning, while appropriate for contingency planning, was believed by many to be too constraining when faced with an actual spill. Acknowledging these limitations and recognizing that CERA may not be appropriate in other regions of the world, IPIECA and

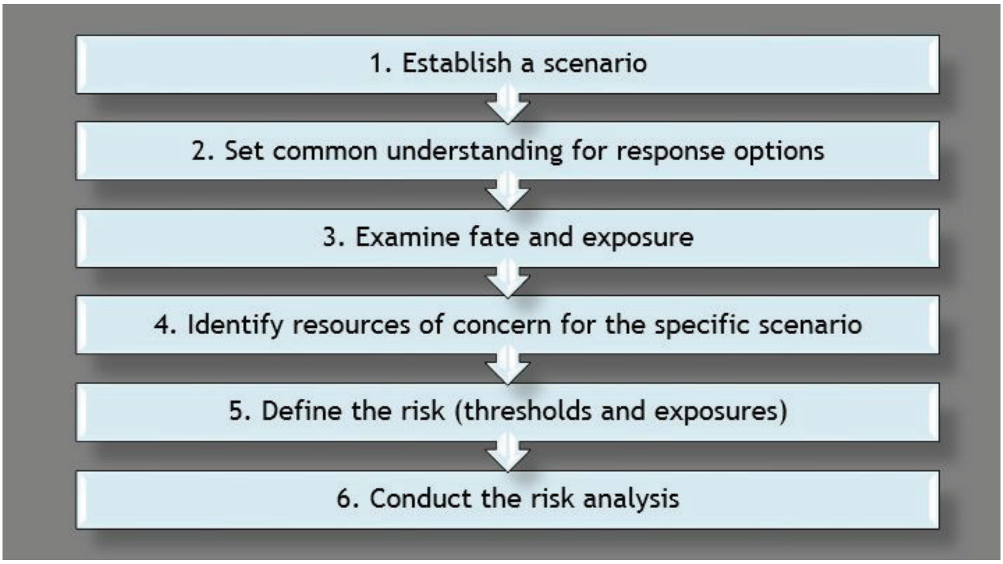


FIGURE 5.6 A simple depiction of the steps in the CERA process. SOURCE: Coelho, 2014.

the International Association of Oil & Gas Producers (IOGP) (IPIECA-IOGP, 2015) released an updated document titled *Response Strategy Development Using Net Environmental Benefit Analysis*. Although both IPIECA documents (2000 and 2015 versions) stressed the importance of making trade-off analyses of response options versus consequences, neither report presented a method to consistently apply a process.

In 2016, IPIECA, IOGP, and the American Petroleum Institute (API) worked together to develop a new method for studying risk in oil spill response that could address challenges in scoring and more readily facilitate stakeholder concurrence in past CERAs. The publication, *Guidelines on Implementing Spill Impact Mitigation Assessment* (IPIECA-API-IOGP, 2017), provided the strategy for analyzing oil spill effects and facilitating response option selection. As part of the refinement and communication process in developing SIMA, this framework was evaluated in workshops in North America (Clean Gulf Conference Workshop on SIMA organized by API/IOGP/IPIECA—October 21, 2016), Europe, and Asia-Pacific (IPIECA workshop in Perth, Australia—November 30-December 1, 2017; IPIECA workshop in Singapore—December 5, 2017; AMSA workshop in Newcastle, Australia—August 6-9, 2018). In addition, two SIMAs were completed in exploration blocks in Eastern Canada in 2017 (Coelho et al., 2017a; Slaughter et al., 2017).

Like CERA, the SIMA tool uses a structured framework for evaluating response options. It involves four steps:

Step 1. Compile and evaluate data

NEBA analysis considers the characteristics of the spilled oil and the transformations it may be subjected to as it weathers and spreads, which may determine the magnitude of environmental, biological, and socioeconomic impacts (Daling et al., 2014). Data linked directly to planning scenarios under consideration primarily include oil properties, oil spill trajectory modeling, environmental sensitivity maps, and identification of appropriate response options for that particular site.

Step 2. Predict outcomes

The data obtained in Step 1 are reviewed and assessed by the planners and responders. Figure 5.7 summarizes the tasks in Step 2 and how they interact with Step 1. SIMA includes an evaluation of the potential effect of a baseline scenario where no response actions are taken, which covers the time scale needed for the oil to be naturally attenuated (IPIECA-IOGP, 2015).

The effects of the response options are characterized and evaluated after baseline establishment. Combined interactions of multiple response technologies at this stage must be considered. During Step 2, the user develops a table of resources versus response options (see Figure 5.8).

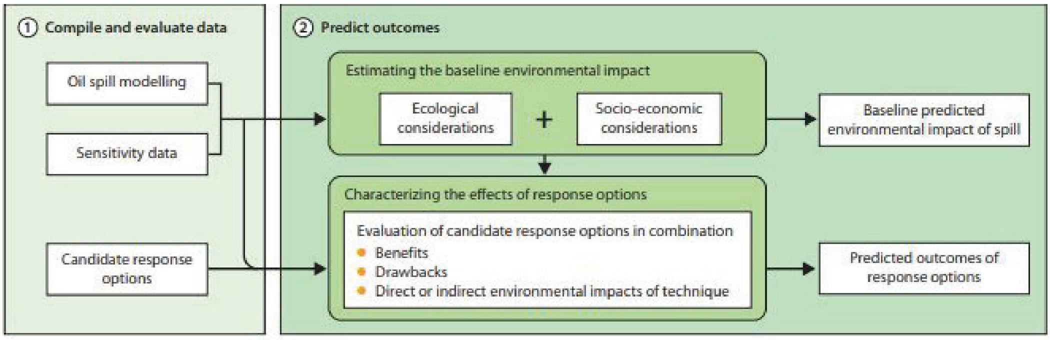


FIGURE 5.7 NEBA Step 2 framework. SOURCE: IPIECA-IOGP, 2015.

RESOURCE COMPARTMENTS	NO INTERVENTION		CONTAINMENT AND RECOVERY		SURFACE DISPERSANT		SUBSEA DISPERSANT	CONTROLLED IN-SITU BURNING		SHORELINE BOOMING	
	Potential relative impact		Impact modification factor	Relative impact mitigation score	Impact modification factor	Relative impact mitigation score	Not feasible for a surface spill	Impact modification factor	Relative impact mitigation score	Impact modification factor	Relative impact mitigation score
		A	B1	A x B1	B2	A x B2		B4	A x B4	BS	A x BS
Seabed	None	1	0	0	0	0		0	0	0	0
Lower water column	None	1	0	0	0	0		0	0	0	0
Upper water column	Low	2	1	2	-2	-4		0	0	0	0
Water surface	Medium	3	1	3	3	9		2	6	0	0
Air	Medum	3	1	3	2	6		1	3	0	0
Shorelines		3	1	3	3	9		2	6	1	3
Saltmarsh *Estuarine mudflats* *Sandy beaches*	*High* *High* *Low*	*4* *4* *2*	*1* *1* *1*		*3* *3* *3*			*2* *2* *2*		*1* *1* *2*	
High value resources	Low	2	0	0	1	2		0	0	1	2
Socio-economic		4	1	4	2	8		1	4	3	12
Boat harbour *Water recreation*	*Medium* *High*	*3* *4*	*1* *1*		*2* *2*			*1* *1*		*2* *3*	
Cultural	None	1	0	0	2	2		1	1	1	1
	Total impact mitigation score:			1S		32			20		18
	Ranking:			**4th**		**1st**			**2nd**		**3rd**

FIGURE 5.8 Overview of Step 2 and Step 3. SOURCE: IPIECA-API-IOGP, 2017.

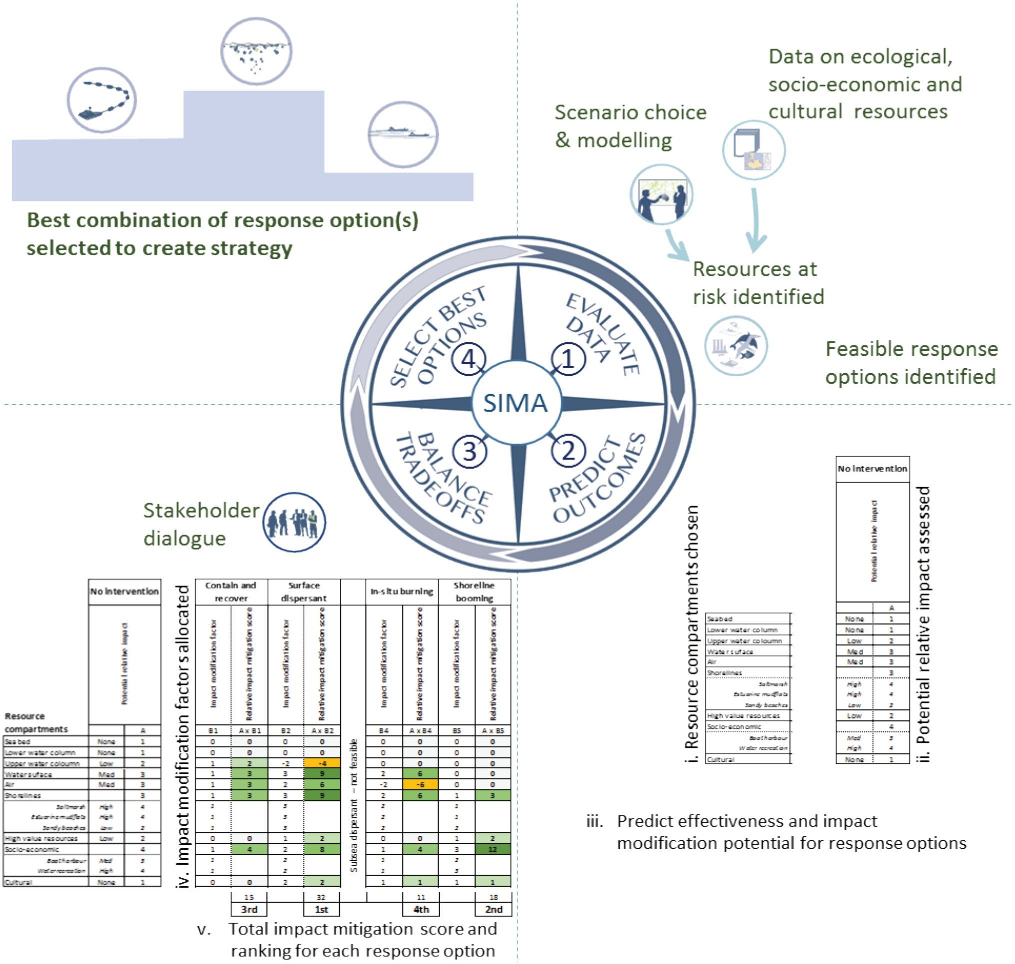
Step 3. Balance trade-offs and reach consensus

This step requires a range of stakeholders to reach consensus on the relative priority of the environmentally sensitive resources and to understand the trade-offs associated with available response technologies (ASTM, 2013a; IPIECA-IOGP, 2015). Two trade-off aspects are balanced in this step (i.e., protection and response and the benefits and drawbacks of selected response options). For the former, this priority may be influenced by the ease of protection and response; recovery times; and the importance for subsistence, economic value, and seasonal changes (IPIECA-IOGP, 2015).

Step 4. Select the best options

Following evaluation of all data, expert opinions, and identified trade-offs, the final step is focused on the selection of the optimum response strategy for both the planning scenario and the prevailing spill conditions. Prior to a spill, response strategies may be identified for various planning scenarios. During a spill, the deployment and adjustment of response capacities may be needed. After spills, the process supports the decisions about when response endpoints have been satisfied by continuing monitoring of response effectiveness and evolving conditions (IPIECA-IOGP, 2015).

A visual framework depicting the pathways of decision making is provided in Figure 5.9.



Resource compartments	No intervention Potential relative impact	
		A
Seabed	None	1
Lower water column	None	1
Upper water coloumn	Low	2
Wate r suface	Med	3
Air	Med	3
Shorelines		3
Saltmarsh	*High*	*4*
Estuarine mudflats	*High*	*4*
Sandy beaches	*Low*	*2*
High value resources	Low	2
Socio-economic		4
Boat harbour	*Med*	*3*
Water recreation	*High*	*4*
Cultural	None	1

Resource compartments	No intervention Potential relative impact		Contain and recover Impact modification factor	Contain and recover Relative impact mitigation score	Surface dispersant Impact modification factor	Surface dispersant Relative impact mitigation score		In-situ burning Impact modification factor	In-situ burning Relative impact mitigation score	Shoreline booming Impact modification factor	Shoreline booming Relative impact mitigation score
		A	B1	A x B1	B2	A x B2	Subsea dispersant – not feasible	B4	A x B4	B5	A x B5
Sea bed	None	1	0	0	0	0		0	0	0	0
Lower water column	None	1	0	0	0	0		0	0	0	0
Upper water coloumn	Low	2	1	2	-2	-4		0	0	0	0
Water suface	Med	3	1	3	3	9		2	6	0	0
Air	Med	3	1	3	2	6		-2	-6	0	0
Shorelines		3	1	3	3	9		2	6	1	3
Saltmarsh	*High*	*4*	*1*		*3*			*2*		*1*	
Estuarine mudflats	*High*	*4*	*1*		*3*			*2*		*1*	
Sandy beaches	*Low*	*2*	*1*		*3*			*2*		*2*	
High value resources	Low	2	0	0	1	2		0	0	1	2
Socio-economic		4	1	4	2	8		1	4	3	12
Boat harbour	*Med*	*3*	*1*		*2*			*1*		*2*	
Water recreation	*High*	*4*	*1*		*2*			*1*		*3*	
Cultural	None	1	0	0	2	2		1	1	1	1
				15		32			11		18
				3rd		**1st**			**4th**		**2nd**

FIGURE 5.9 SIMA decision framework. SOURCE: IPIECA, 2017.

COMPARATIVE RISK ANALYSIS

A CRA seeks to compare the benefits and consequences (effects/impacts on biota) of various response options. In many ways, it can be considered an evolutionary step of NEBA, one that takes advantage of recent advances in biological modeling technology to remove some of the subjectivity out of preceding frameworks. To date, there has been only one attempt at a CRA. It focused on a DWH-like blowout in the deep water of the Gulf of Mexico (Bock et al., 2018; French-McCay et al., 2018a; Walker et al., 2018a) and was extended to examine the sensitivity of the fates to changes in site location (including depth) and droplet size (French-McCay and Crowley, 2018). As a newly developed framework, a key rationale of the CRA is that it attempts to reduce uncertainties introduced through the use of integrated models, whose predicted results may not reflect actual occurrences in the environment, by comparing the relative risks and benefits of various response options.

At the core of a CRA is an integrated model that is capable of simulating both the fates and the effects of a spill. In the case of the CRA study by French-McCay et al., the SIMAP/OILMAP DEEP models were used, but the methodology could be employed, of course, with other models such as the OSCAR/ERA-Acute model (Libre et al., 2018). The fate component of SIMAP has been around for several decades and has evolved in terms of complexity. The basic output from the fate component is a 4-D concentration map of hydrocarbon constituents. The 4-D fields of concentrations from the fate component is used to estimate hydrocarbon *effects* on important biota. Given our incomplete understanding of ecosystems, modeling biological effects even for a few important species, groups, or habitats is challenging.

Perhaps the most difficult and potentially controversial task is the final step, which involves weighting the relative importance of the species under consideration. Bock et al. (2018) described a method they developed, which used elements of a SIMA/CERA. In the context of an SSDI application, they concluded that SSDI provided more benefits than costs and that the trade-off analysis was insensitive to the weighting of their important species. In other words, the positive effects of using SSDI overpowered the negative consequences regardless of how one valued the biota affected by the spill. These results will be explored more thoroughly in Chapter 6 in the case of comparing SSDI to other response options.

ECOSYSTEM SERVICES

As described by the NRC (2013), ecosystem services (ES) are the goods and services supplied to humans by natural resources. Examples of economically important ES in the Gulf of Mexico include commercial fish and flood control (due to wetlands). Less quantifiable ES include climate regulation and water purification. The idea of an ecosystem services analysis (ESA) was introduced in the early 1980s (Ehrlich and Mooney, 1983), and it has continued to slowly evolve. By far the most ambitious ESA was started by the United Nations in 2000 to evaluate present and future conditions of major ecosystems and to estimate the consequences of ecosystem change to humans (Millennium Ecosystem Assessment, 2005).

Applying an ES approach requires two major components: (1) reasonable models of important physical and biological systems for the region of interest, and (2) economic models (what economists refer to as "production functions") that convert the physical and biological effects into a monetary value. In its simplest conceptual form, the physical/biological models would track the consequence of an oil spill on the local ecosystem services (e.g., fish populations) and quantify those in terms of a 4-D series of some important metric (e.g., tons of fish). This output would factor into the production function to calculate an economic effect.

The NRC (2013) explored conceptually the use of an ESA to estimate the damage of the DWH spill as an alternative to the traditional methods used in a Natural Resource Damage Assessment. They concluded that an ESA could theoretically improve the fairness of financial compensation to human victims and more efficiently guide restoration of the most valuable resources. That said, the report noted the many obstacles that inhibit an ESA, notably the inability to accurately model the effect of an oil spill on important ecosystems and to quantify those effects from a financial standpoint.

In this context, it is apparent that the application of ES principles to the assessment tools (i.e., CERA, SIMA, and CRA as it matures), rather than using "length of recovery" of a particular species, is a natural next step in their evolution. While an ESA may not be appropriate for response option analysis during small oil spills, it is reasonable to expect that an ESA might become a valuable tool for dispersant-use decision making at larger, offshore oil spills.

FINDINGS AND RECOMMENDATIONS

Finding: The objective of the Net Environmental Benefit Analysis (NEBA) process is to conduct an evaluation that will allow spill responders and stakeholders to evaluate the trade-offs involved with the various response options and choose the option(s) that will result in a reduction of potential adverse impacts and/or the best overall recovery of the ecological, socioeconomic, and cultural resources of concern, while satisfying the primary goal of minimizing immediate risks to response workers and public health and safety.

Recommendation: Decisions should be based on a balanced evaluation of consequences not driven by specific individuals, species, or economic interests.

Recommendation: Greater efforts should be taken to expand and highlight the effects on human health and safety in the decision-making tools.

Finding: All three decision-making tools—Consensus Ecological Risk Assessment (CERA), Spill Impact Mitigation Assessment (SIMA), and Comparative Risk Assessment (CRA)—have value and can be used in support of contingency plan development, strategic planning during the initial stages of a spill response, or tactical execution during the active phase of a response.

Recommendation: Decision makers should further evaluate surface and subsea spill scenarios using NEBA tools (i.e., CERA, SIMA, or CRA) to better define the range of conditions (e.g., oil type, sea state, depth, location, resources at risk) where dispersant use may be an appropriate and/or feasible response option for reducing floating oil.

Recommendation: The NEBA tools (CERA, SIMA, and CRA) should be expanded to consistently address the health of response personnel, community health, and socioeconomic considerations (e.g., beach closures). Furthermore, these tools should be used to gain stakeholder input on local or regional priorities, to expand awareness, and to gain trust in the decision-making process.

Finding: The complexity of the interactions among fates and effects can be best addressed using numerical models. However, expert opinions used in the CERA and SIMA processes provide valuable insight into many trade-off decisions, and this risk communication process allows for consensus by all stakeholders.

Recommendation: Response decision making should seek to become more quantitative to improve evaluation of the ecosystem services of the whole impacted region.

Finding: The NEBA process is best achieved by using a blend of information provided by numerical models and stakeholder input.

Finding: Integrated models that calculate the fates, as well as effects, of an oil spill are now available, and most of the sub-models upon which they are based have been validated.

Recommendation: A controlled field experiment or spills of opportunity should be used to collect comprehensive field observations for validating the entire integrated model.

Recommendation: Integrated models should be used to evaluate and optimize combinations of response options.

Finding: Integrated models are routinely used in tactical and strategic oil spill planning, usually with limited insight into their uncertainty bounds.

Finding: It is important for end users of numerical models to understand that even the best models have uncertainties.

Recommendation: Systematic studies of the uncertainty bounds in integrated models are needed, and methods should be developed to include these bounds as a routine model product. Tools are also needed to help decision makers quantitatively account for this uncertainty in a consistent manner.

CHAPTER 6

COMPARING RESPONSE OPTIONS

INTRODUCTION

Every marine oil spill is distinct, each with its own set of unique conditions and complexities. Oil spills may result from a variety of incidents—ranging from platform blowouts to tanker collisions—and the location, time of year, duration, depth, environmental conditions, affected biomes, and available response resources may all vary significantly. This diversity challenges responders to be adaptive to the particular circumstances of a spill and has led to the development of multiple marine oil spill response options. Current commonly used, open-water response methods include mechanical recovery of oil using skimmers and booms; in situ burning of oil at the surface; monitored natural attenuation; and enhanced dispersion of oil through the application of dispersants, either at the surface or via subsea injection. As will be discussed further, each method has advantages and disadvantages (see Table 6.1), and the determination of which method, or set of methods, to employ requires consideration of the spill conditions as well as any trade-offs associated with each technique. Additionally, the volume of oil that can be treated per unit time (i.e., the encounter rate) is evaluated, taking into account both the thickness and concentration of the oil and the speed that a particular method can interact with the oil. The use of bioaugmentation, biostimulation, enzyme addition, and solidifiers is not considered in detail because these methods have not been used to a significant extent, especially when considering a large-scale, open-water spill response. Note that biostimulation and bioaugmentation have been tried a number of times in nearshore and shoreline environments and even a few times offshore. They were proposed (but not implemented) during the *Deepwater Horizon* (DWH) oil spill, tested during the Ixtoc I spill, and recently tried at several spills in Europe. However, the testing and understanding of the biostimulation and bioaugmentation approaches are too limited to provide detailed descriptions in this text.

After presenting the advantages and disadvantages of individual approaches, this report examines special considerations and compares the results of using different response methods on the environment. As shown in Chapter 5, the decision-making process involves many factors. There are rarely opportunities to study the differences in environmental effects to the use of the different

TABLE 6.1 Operational Summary of Open Water Response Options

Response Option	Benefits	Limitations
Surface Dispersant Application	• High aerial coverage rate possible at the water surface • Large volumes of oil can be treated • Reduced vapors at the water surface; improves workers' safety • No recovered oil storage requirements • Lower manpower requirements • Reduces the potential for oil reaching the shoreline • Enhances natural biodegradation • Useful in higher wind and sea conditions • Effective over wide range of oil types and conditions	• Special approvals required • May not work in calm seas • Light and water depth limitations • Short-term, localized increase in toxicity • Potential impact on water column resources • Specialized equipment and expertise required • May not be as effective on high viscosity fuel oils • Has a limited "window of opportunity" for use • Relies on biodegradation to remove oil from the ecosystem • Public perception
Subsea Dispersant Injection	• Large volumes of oil can be treated with high efficiency • Lower dispersant-to-oil ratios can be used • Reduced vapors at the water surface; improves safety • Oil dispersed through a larger portion of the water column • Lower manpower requirements • Reduces the potential for oil reaching the shoreline • Useful in wind and sea conditions that would inhibit other response options • Effective over wide range of oil types and conditions • Applications can be performed continuously—24 hours, 7 days per week	• Less known about long-term effects of subsea use • Potential impact on water column resources • Localized increase in toxicity and reduction in oxygen • Special approvals required • Specialized equipment and expertise required • It is difficult to monitor dispersant effectiveness • Relies on biodegradation to remove oil from the ecosystem • Public perception
At-Sea Mechanical Recovery	• Permanently removes oil from the water • Well-accepted, no special approvals needed • Effective for recovery over wide range of spilled products • Large "window of opportunity" • Greatest availability of equipment and expertise • Recovered product may be reprocessed	• Inefficient and impractical on thin slicks • Is limited by weather, sea state, and light • Requires storage capability • Typically recovers no more than 10% of the oil spilled in open ocean environments, more may be recovered in other conditions • Labor and equipment intensive • Large volumes of oily waste
Controlled In Situ Burning	• High oil elimination rate possible • No recovered oil storage requirements • Effective over wide range of oil types and conditions	• Requires fresh oil with volatile components • Special approvals and permits required • Ineffective in inclement weather or high sea state • Black smoke perceived as significant impact on people and the atmosphere • Localized reduction of air quality • Specialized equipment and expertise required • Burn residue may sink or be difficult to recover

TABLE 6.1 Continued

Response Option	Benefits	Limitations
Monitored Natural Attenuation	• No intrusive removal or response techniques that further damage the environment • May be best option if there is little to no threat to human or environmental well-being • When selected for certain areas and conditions, the environment can recover from the spill more effectively than it might when using other response tools	• Winds and currents can change, sending the oil spill toward sensitive areas • Residual oil can impact shoreline ecology, wildlife, and economically relevant resources • Public perception that responders are doing nothing • Allowing the oil to weather beyond a certain point will render other response methods less effective or ineffective • Predictions of oil fate and effect require careful monitoring, detailed baseline data, and adequate experience with predictions

SOURCE: Modified from Coelho, 2013, and IPIECA et al., 2015.

response options. Therefore, responders often rely on integrated models to predict the effects of various response options.

SUMMARY OF KEY OFFSHORE RESPONSE OPTIONS

An optimal offshore spill response will likely require a combination of the response methods discussed above, which are often constrained by physical conditions, prevailing weather, and safety considerations. An International Union for Conservation of Nature report on evaluating oil spill response highlights the importance of considering the resources to be protected, the effectiveness of different response options, and the possible impacts of the response itself (Stevens and Aurand, 2008).

SURFACE DISPERSANT OPERATIONS

Overview

As discussed in Chapter 1, there are managed stockpiles of several well-studied dispersant products located around the world. There are also dispersant delivery systems (e.g., boat spray systems, coiled tubing, aerial dispersant tanks and spray arms) and platforms (vessels, aircraft, subsea equipment) located strategically to provide support in the event of a spill. In general, these products, systems, and platforms have been designed to deliver dispersant to an oil spill as effectively as possible with an understanding of the requirements of product safety and stability, government regulations, effectiveness on a range of crude oils, and specific hardware.

Dispersants are applied to surface waters from airplanes, helicopters, or boats. Dispersant spray systems are intended to provide a droplet size distribution (DSD) that minimizes misting of small droplets and slick penetration from larger ones. The dispersant-to-oil ratio (DOR) can be adjusted to actual field conditions from an initial rule of thumb value of 1:20 (or 5%) taking into consideration oil type, weathering, and slick thickness.

Natural processes (e.g., wind and wave action) mix the dispersant-treated oil into the top few meters of the water column. The small dispersed oil droplets (generally 10-100 microns [μm]) remain suspended in the water column and are an indicator of dispersant effectiveness (Li et al., 2009a,b; Lunel, 1993). While the larger naturally dispersed oil droplets are more buoyant and rise back to the surface, smaller chemically dispersed droplets are less likely to re-coalesce, and instead form more stable oil-in-water emulsions. The dispersed oil droplets dilute (vertically and horizontally) within the water column and begin to dissolve and biodegrade. Initial dispersed oil water column concentrations of 10 to 50 parts per million (ppm; see Box 6.1) have been measured in the top 10 m under a slick (Lee et al., 2013a), and these concentrations continue to rapidly decrease within several hours (NRC, 2005; OSAT, 2010).

Benefits

Dispersant application from aircrafts can treat large volumes of oil over a large area. Application can be performed in higher wind and sea states than other response options that require mechanical containment. The ability to rapidly treat large volumes of spilled oil reduces the impact to wildlife at the ocean surface and on shorelines and can improve worker safety by reducing chemical vapors at the ocean surface. The application of dispersants to a surface slick can result in rapid dilution to very low concentrations. Additionally, under favorable conditions, dispersed oil droplets may begin biodegrading more quickly, because the smaller droplets provide a larger surface area for microbial action, which would facilitate more rapid removal from the environment.

Limitations

Special approvals may be required to apply dispersants. Regulatory authorities may require a minimum water depth and application distance from shore, and they may establish other exclusion zones or conditions. Aerial operations are restricted to daylight hours and typically require 3 statute miles of visibility, a minimum cloud ceiling of 1,000 feet, and wind speeds below 35 knots to ensure aircraft safety. In the case of vessel-based dispersant application, operational limitations associated with energetic sea states and corresponding concerns for responder safety need to be taken into consideration. Dispersant application requires specialized equipment and expertise to apply and has a limited "window of opportunity" as the surface slick continues to weather. Surface dispersant application may be less effective in calm waters and with more viscous oils, although studies have shown that dispersants stay with floating oil for an extended period of time, during which environmental conditions are likely to change (Huber et al., 2014; Nedwed et al., 2006). Other studies have examined dispersion of a range of heavier oils, some of which dispersed effectively (Belore et al., 2008). Ultimately, the removal of dispersed oil from the water column is dependant on biodegradation.

BOX 6.1
Concentrations of Dispersed Oil After Dispersant Use

Previous studies and spills have demonstrated that, for surface dispersant operations, dispersed oil concentrations generally range from 10-50 ppm in the top few meters of the water column for the first hour following dispersant application. Rapid horizontal and vertical mixing then quickly reduces the concentration of dispersed oil to below 1 ppm. These processes were evident in both the *Deepwater Horizon* (DWH; also referred to as the Macondo spill) oil spill (OSAT, 2010) and past North Sea field experiments conducted in the mid-1990s (AEA Technology, 1994, 1995; Jones and Petch, 1995; Slaughter et al., 2017; Strøm-Kristiansen et al., 1997).

During DWH, dispersed oil concentrations were monitored throughout the response because subsea dispersant injection was used almost continuously. Subsea dispersant monitoring was not permitted close to Source Control, due to a 1 km radius exclusion zone from the wellhead. Outside of the exclusion zone, a subsea dispersed oil plume was detected at depths of approximately 1,100-1,300 m. This plume was typically narrow and was transported away from the site by subsea currents. Within that plume, dispersed oil concentrations were typically very low—in the 100 ppb to several ppm range (NOAA, 2012; Slaughter et al., 2017).

Effectiveness

The type of oil and environmental conditions present during the spill event will influence the effectiveness of the dispersant operation. Effectiveness is defined as the percent ratio of the amount of dispersed oil to the oil remaining at the surface after treatment and can approach 100%, especially for fresh, un-weathered oil. The overall effectiveness is influenced by the extent of oil weathering and its composition, available mixing energy, the type and amount of dispersant, water temperature, and salinity (Chandrasekar et al., 2006; Li et al., 2010; Mukherjee, 2008; Mukherjee et al., 2011; NRC, 2005). While oil components such as resins, asphaltenes, and larger aromatic compounds or waxes may be poorly dispersible, oil components such as saturates (major components in diesel fuel) will both naturally and chemically disperse. As mentioned, surface mixing energy is supplied mostly from waves and wind, and lower volumes of surface dispersant are generally required in higher sea state conditions to achieve desirable levels of dispersion (NRC, 2005). Though most crude oils and many petroleum-based fuels and lubricants can be dispersed initially, dispersant effectiveness will gradually decrease as the extent of oil weathering proceeds (IPIECA-IOGP, 2015), that is, loss of volatile components and formation of stable water-in-oil emulsions (Daling et al., 1990; Lewis et al., 1995; Payne and McNabb, 1984).

Even though chemically dispersed oil may have a different appearance due to the small droplet size, effectiveness can be difficult to verify in the field because the dispersant action may occur over an extended period of time, and wind and currents may transport the oil away from the application area. Additionally, the establishment of safety offsets for on-water personnel during aerial dispersant application may mean that significant time periods occur before in-water evaluation of dispersant effectiveness may be made. Visual observation of aerial dispersant effectiveness can be affected by such factors as weather, visibility, and daylight, so it is important that trained observers are deployed. The National Oceanic and Atmospheric Administration's Dispersant Application Observer Job Aid mentions that no color change may be associated with dispersant application (NOAA, 2007). Therefore, definitive determination of dispersant effectiveness (whether at the surface or subsea) by measurement of fluorescence of specific crude oil components or laser light scattering from dispersed oil droplets should be used to augment visual observations.

A number of laboratories have evaluated dispersant effectiveness using a variety of test methods with known amounts of dispersant, reference oil, and water in an enclosed vessel under known energy mixing rates (Venosa et al., 2002). Summaries of a number of these dispersant effectiveness tests and comparisons of their results with different crude oils are widely available (see, for example, Holder et al., 2015). The results of laboratory tests are highly influenced by mixing energy and settling time as large oil droplets tend to resurface, especially in the closed systems employed by the specific tests. Thus, test methods measuring effectiveness during mixing are likely to indicate a higher level of effectiveness than are methods that measure effectiveness after a period of settling. In practice, while the measurement of the surface removal ratio of oil in the laboratory is useful for the relative comparison of products, it is not likely to reflect effectiveness values under operational conditions—particularly wave conditions—in the open ocean where there is significant potential for dilution and dispersed droplets are not likely to re-coalesce into a surface slick.

As a result of studying oil droplet size in the water column and the changes that occur when dispersants are used, it has been recommended that the DSD be used as an essential parameter to evaluate the spill response and the long-term behavior of the oil (NRC, 2005). While oil droplets in the water column retain their natural buoyancy, smaller droplets travel through the water column much more slowly as a result of the physics associated with their different sizes: namely, larger droplets tend to resurface and smaller droplets remain entrained in the water column for extended periods (Boufadel et al., 2006, 2007; Chen and Yapa, 2007).

Technological Advances

A review of improvements in dispersant technology is provided by Rowe et al. (2017). The main areas of focus on improving/enhancing surface dispersant operations have included

- New dispersant formulations and/or approaches to dispersing oil. For example, products are being considered that may have less solvent for higher effectiveness, use plant-sourced components as alternate raw materials, or consider different mechanisms such as the formation of Pickering emulsions or the use of mechanical energy to form small droplets (Brandvik et al., 2014a; Guo, 2014; Katepalli et al., 2017; Nedwed, 2011).
- New delivery systems such as the recently certified Boeing 727-based aerial platform introduced by Oil Spill Response, Ltd., which provides a global reach and an extended range of daily operations (Caetano and White, 2017).
- Gaining a better understanding of factors influencing dispersant/oil slick interactions such as the impact velocity of dispersant droplets of different size following release from spray systems (Ebert, 2008).

SUBSEA DISPERSANT INJECTION (SSDI)

Overview

The response to the 2010 DWH oil spill is the first case where dispersants were applied at the wellhead on the seafloor. There are a few key distinctions between surface and subsea conditions. Near the release source, significant turbulence resulted in the jet of oil and gas breaking into a wide range of oil droplet and gas bubble sizes (Malone et al., 2019; Pesch et al., 2018). The use of SSDI (see Figure 6.1) is focused at the release point. Here, the encounter rate with the oil can be maximized with the intention of reducing droplet sizes to delay and perhaps even to stop the ascent of the droplets, thereby facilitating the biodegradation process.

Benefits

The encounter rate with SSDI is potentially higher at the oil release point, compared to aerial dispersant application to a spreading surface slick, because the dispersant is applied directly to the oil source as it enters the ocean. Because of this, lower DORs are expected to be sufficient to effectively disperse the oil, with values of 1:100 (1%) or less having been demonstrated successfully in the laboratory (Brandvik et al., 2013, 2014a,b, 2017a, 2018, 2019a,b). The trajectory of rising oil from depth is influenced by deep ocean currents (horizontally) and the buoyancy of the dispersed oil droplets (vertically). This leads to the dispersed oil being vertically distributed over a greater depth range than would occur with surface application, which is limited to the top few meters of surface water. Biodegradation will occur in these cold deep waters. Measured dispersed oil concentrations were consistently below 5 ppm at a distance of 1 km from the DWH wellhead (Coelho et al., 2011). SSDI can run continuously in almost all weather conditions, using a DOR that is less than half the volume typically needed for surface applications (IPIECA-IOGP, 2015). The operation takes place at a single location at the wellhead release point, which simplifies the operation (compared to surface dispersant use). This makes SSDI more manageable and reduces manpower requirements and safety concerns compared to other response methods.

SSDI may reduce the potential for responder exposure to hydrocarbon vapors at the surface (Gros et al., 2017; see Chapter 4), which provides a worker health protection factor. In support of this, a recent Comparative Risk Assessment (CRA) project involving several modeled scenarios concluded that SSDI substantially decreased surface slicks and shoreline oiling; increased

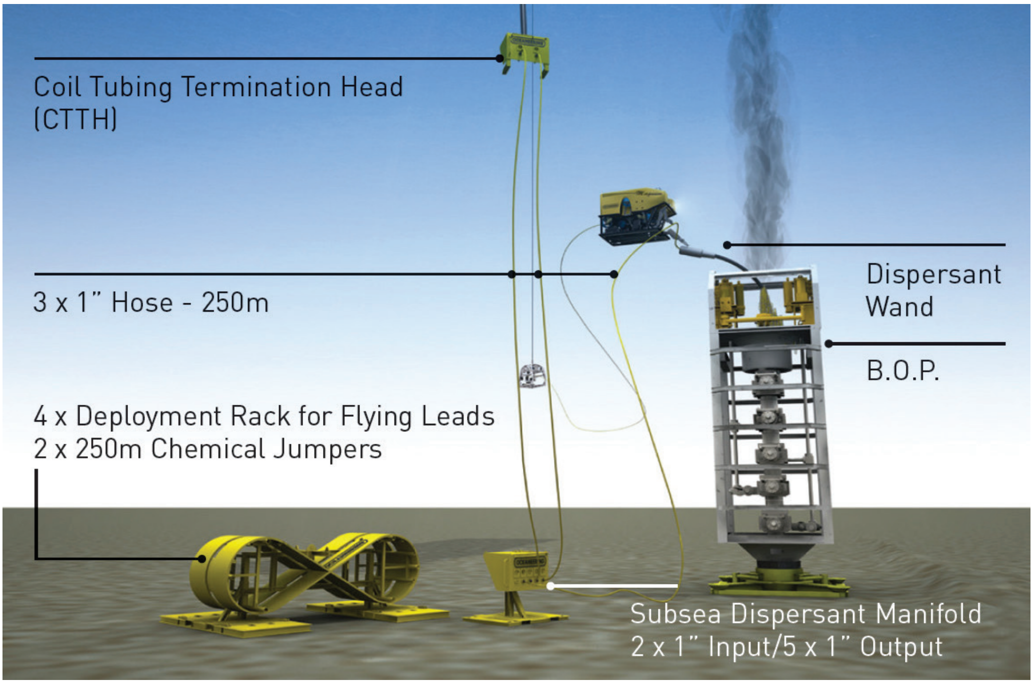


FIGURE 6.1 A closer look at the specific elements of one configuration of SSDI equipment. The dispersant is pumped from the surface vessel through the coiled tubing to the subsea dispersant manifold, then ultimately through the SSDI wand that is being held by the remotely operated vehicle. SOURCE: Oil Spill Response Limited Subsea Well Intervention Services.

hydrocarbon biodegradation at depth; decreased atmospheric volatile organic compound (VOC) emissions; and increased dissolution rates of rising oil such that floating oil contained much less soluble and semi-soluble hydrocarbons (benzene, toluene, ethylbenzene, and xylene; polycyclic aromatic hydrocarbons [PAHs]; soluble alkanes). These factors reduced human and wildlife exposures to VOCs (French-McCay et al., 2018b).

Unlike most other operations, SSDI can progress continuously through day and night provided that required dispersant volumes can be supplied to the site. The SSDI reduces the amount of oil reaching the surface and thereby reduces the potential for oil to reach the shoreline or impact birds and mammals.

Limitations

Because SSDI has been used only once, less is known about the biological and long-term impacts on the ecosystem than for other responses. Localized increases in toxicity within the water column are expected due to enhanced oil bioavailability from droplet formation, and as the oil is biodegraded, a measurable reduction in dissolved oxygen has been reported (Kessler et al., 2011a; see Figure 6.2).

Aerobic biodegradation is a key process for removing dispersed oil from the ecosystem by transforming hydrocarbons to CO_2 and water, but depending on site-specific conditions, concentration of dispersed oil, nutrient levels, etc., there may be mitigating circumstances where it is less effective. For example, suspended droplets may be incorporated into marine snow and carried to the seafloor (Passow, 2016; see Chapter 2) where they may biodegrade more slowly or impact

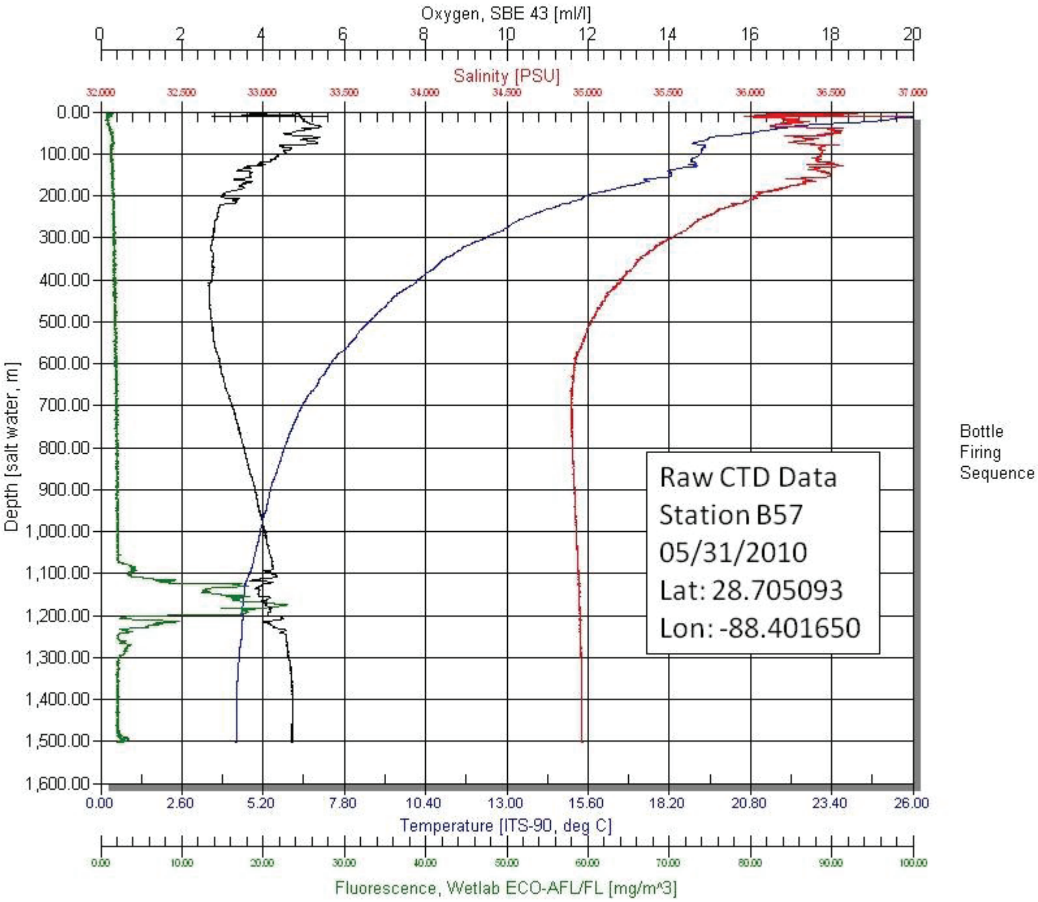


FIGURE 6.2 Depth profile highlighting a hydrocarbon intrusion layer as observed during the DWH spill, including colored dissolved organic matter fluorescence (a proxy measurement sensitive to MAHs and PAHs), dissolved oxygen, and density. These downcast data were collected on May 31, 2010, at a station located 5 km SW of the wellhead while SSDI operations were occurring. Note the peak in fluorescence at depths of 1,100 to 1,200 m and the commensurate sags in dissolved oxygen. A smaller fluorescence peak is also apparent near the bottom of the downcast at 1,500 m. SOURCE: Coelho et al., 2011b.

benthic organisms. In general, there is less known about the biota at depth to judge the potential impacts of dispersed oil on the ecosystem.

In deepwater spills it may be difficult to monitor the effectiveness of the dispersant, although instruments and procedures have been developed post-DWH (API, 2013). Furthermore, while SSDI may be effective in some shallow-water spill scenarios, it may not offer substantial benefits in shallow blowouts (see CRA-2 case study below). As with surface application, specialized equipment is required, and special approvals may be required. The application of dispersants, even at depth, can be perceived negatively by the public.

Effectiveness

Recent laboratory testing on light crude oils suggests that in cases where proper injection methods and DORs are used, SSDI effectiveness may approach 100%. For comparison, surface dispersant application typically begins at a DOR of 1:20 (5%), whereas DORs ranging from 1:50 to 1:100 (2% to 1%) can be effectively used with SSDI (Coolbaugh and Cox, 2015). This is due to the higher encounter rate of dispersant directly to the freshly released oil stream, where the oil is warm (low viscosity), not emulsified, and in a region of high turbulence. For the purposes of offshore spill planning, subsea dispersant "application efficiency" is typically assumed to be 80%, meaning that 20% of the dispersant is lost and the remaining dispersant volume treats the oil with 100% efficiency. This simplified assumption provides a conservative estimate of the potential environmental impacts that might occur in the water column.

SSDI effectiveness is visually evident to trained observers looking at real-time video feeds provided by remotely operated vehicle-mounted video cameras positioned adjacent to the dispersant injection wand, but this is purely a qualitative indicator. Quantitative confirmation of droplet size reduction can be obtained via a particle size analyzer located above the dispersant injection point (e.g., Davies et al., 2017). Laboratory studies have demonstrated significant changes in the appearance and DSD of subsurface oil releases (Brandvik et al., 2014a; Coolbaugh and Cox, 2015).

Technological Advances

While subsea dispersant application is not a new concept, its use during the DWH response represents the only documented example of an application at such a scale and depth (IPIECA-IOGP, 2015). A number of lessons were learned from the extended use during the response, and projects have been undertaken to

- Better understand factors that influence dispersed oil droplet size—for example, dispersant type, DOR, oil type, and mixing energy (Brandvik et al., 2013, 2014a,b, 2018, 2019a,b);
- Develop a bench scale effectiveness test in order to facilitate the screening/testing of new products and conditions in an efficient manner (Coolbaugh and Cox, 2015); and
- Recommend scientific protocols to monitor environmental effects of SSDI use (NRT, 2013).

AT-SEA MECHANICAL RECOVERY

Overview

Mechanical containment and recovery is the process of physically removing oil from the water surface through the use of equipment such as skimmers and booms to divert and collect it. Upon its collection, this oil is either disposed of or, in some cases, it may be possible to recycle it, thereby preventing or minimizing effects to sensitive nearshore and offshore habitats. Environmental conditions such as hours of daylight, winds, and waves will influence the success rate of on-water mechanical containment and recovery. In most instances, mechanical recovery is the primary or preferred treatment option.

Benefits

This response option physically removes surface oil from the water, and it is the only option able to remove weathered oil. As a result, public understanding and acceptance of use of on-water mechanical recovery is high. When floating oil is collected in the offshore environment, the potential threat to nearshore and shoreline ecosystems can be significantly reduced because less oil is available to become stranded and the need for shoreline protection and recovery operations is likely to be reduced or even eliminated. During offshore recovery operations, there tends to be little wildlife impact. Also, mechanical recovery is a commonly practiced response option that offers a wide range of well-understood equipment options. In some cases, the recovered product can be reprocessed for later use.

Limitations

While mechanical recovery is a desirable spill response tool, it requires the availability of vessels that can deploy the equipment and have sufficient recovery and storage capacity. Support vessels may have a limited capacity resulting in a significant period of elapsed time (i.e., days) before mechanical recovery can be performed on a large scale. Once on the sea surface, spilled oil has a tendency to spread and form thin sheens, which significantly reduces the ability to collect surface oil efficiently. The longer the spreading process continues, the thinner the oil will become and the less likely it is that it will be recovered. With traditional boom, vessel speeds are restricted to less than a knot to prevent oil entrainment, which limits encounter rates. Some types of skimmer systems may collect large volumes of water with the oil, requiring further oil–water separation after collection, additional equipment, and storage capacity. Waste from all the equipment used, particularly absorbent materials and oily debris, represent a waste management challenge.

The low encounter rate of mechanical systems makes it labor and equipment intensive to mount an effective spill response. In addition to the actual encounter rate, external conditions such as weather and hours of daylight can limit mechanical response. Ocean boom begins to experience containment failure when sea states approach wave heights higher than 2 m. While day length is not a major consideration in the continental United States, limited daylight during the winter months in northern latitudes may reduce the number of operations that can occur each day. Floating ice poses an additional constraint in Arctic waters. Finally, skimmer system configurations may need to change as the oil becomes more weathered, which can result in response delays.

Effectiveness

Mechanical recovery in the offshore environment is affected by weather conditions, the extent of oil weathering, and the actual encounter rate. Even under favorable conditions, experience from previous offshore spills has shown that recovery rates of between 5% and 10% of the total volume are the maximum to be expected—the rest being lost to the atmosphere, the ocean, or deposited on a beach. During the DWH spill response the estimate was less than 4% (Federal Interagency Solutions Group, 2010).

Technological Advances

Mechanical containment and recovery techniques have been used for quite some time, but there continue to be improvements. As an example, innovative enhancements to oleophilic skimmer designs have served to increase potential recovery rates significantly, either by incorporating grooves into disc and drum design (Broje and Keller, 2006) or by the addition of high surface area fabric to skimmer surfaces (Hobson, 2013; SL Ross, 2008). A key focus of the spill response research community is increasing the ability to operate at higher vessel speeds or in faster currents. A particular approach has been to incorporate a calm area at the apex of a boom that prevents entrainment and oil loss from the boom even at 3-5 knots tow speed (USCG, 2002). By pairing such a containment system with paravane, it becomes possible to operate at higher speeds with only one vessel (Chopra and Coolbaugh, 2016).

CONTROLLED (IN SITU) BURNING

Overview

The process of employing in situ burning (ISB) during an offshore oil spill response consists of the mechanical collection of oil in a manner similar to on-water recovery, but it uses specially designed fireproof booms, followed by its removal through burning. The oil must be sufficiently thick in order to initiate ISB. This spill response option has a possible advantage over mechanical recovery in that it removes the need to store and dispose of recovered oil. As in mechanical containment and recovery, ISB has similar operational limitations associated with weather and daylight hours because it relies on the use of a boom-based system. In practice, ISB is optimally performed during daylight hours so that the burn may be safely ignited, managed, monitored, and tracked. Wave heights of less than 1.2 m, somewhat lower than for mechanical containment and recovery, are preferred.

Benefits

ISB can be highly effective at permanently removing encountered oil from the water and reduces the total volume of oil that would need to be collected and disposed. Because most crude oils will burn, ISB can be an effective technique for a wide range of oil spills. Because of its potential effectiveness and reduced requirements for collection and disposal, ISB can serve to minimize the extent of a spill and reduce the resources, including time, required during a response.

Limitations

ISB requires oil that has limited weathering, as the loss of light end components or inclusion of water can prevent the ignition of a burn. The oil must be more than 3 mm thick to allow ignition, making it impractical for thin slicks. In the event that populated areas are present downwind of a burn, air quality concerns may exist in some jurisdictions due to the possible presence of combustion-related gases and particulate materials, especially those of very small size. The black smoke plume is perceived as having a significant impact on people and the atmosphere. As lighter crude oil components burn, burn residues may become more dense and sink into the ocean where they are not recoverable. Optimal ISB performance occurs during daylight hours when the burn may be safely ignited, managed, monitored, and tracked, with wave heights of less than 1.2 m. ISB requires specialized equipment and training. The availability of effective fire boom, which in practice has been found to have a limited lifetime, is a consideration for any large-scale, prolonged response operation such as a well blowout. A key consideration in the decision-making process to use ISB is whether it is feasible with respect to incident specific environmental conditions and existing regional government approval policies; burn plans and special approvals are likely to be required. Many countries have not established ISB approval processes.

Effectiveness

The ISB response tool is highly dependent on the incident-specific environmental conditions and potential encounter rates. A burn can remove oil until a minimum thickness around 1 mm remains. When the oil thicknesses in the boom are greater than 1 centimeter, the burn efficiencies can exceed 90%. During the DWH response, where the sea was quite calm over extended time periods, existing estimates indicate that about 5% of the oil was removed by ISB (Allen et al., 2011; Federal Interagency Solutions Group, 2010).

Technological Advances

Prior to the DWH spill response, ISB had only been used occasionally. Although it had never been used on the scale as that of the DWH response, the technique was studied on a regular basis (Mabile, 2013). The usual method for thickening a slick is to mechanically contain the slick in special fire booms, some of which were refined following the DWH response (IPIECA-IOGP, 2016). While fire booms are able to withstand the heat of a burn for several sustained burns, they will ultimately be unusable after a few days.

To move beyond this limitation, the use of surfactant-based herding agents presents an opportunity to perform ISB without physical containment. By applying these products around the edge of a slick, the surface tension is modified, the slick area contracts, and the oil becomes thick enough to support combustion. This approach has been demonstrated several times, and it has been shown that the slick will remain thickened for several minutes before the herding effect ultimately dissipates, during which time ignition is possible (Buist et al., 2011). The environmental conditions in which herders will be effective are not fully established.

Other work is currently focused on enhancing burn effectiveness by incorporating metallic heat sinks within the combustion zone for more complete combustion and by integrating a skimming/burning system, which would alleviate the need for waste storage or fire-resistant boom in locations with logistical challenges (Rangwala et al., 2015).

MONITORED NATURAL ATTENUATION (NATURAL RECOVERY)

Overview

Natural attenuation involves no active human intervention aimed at changing the fate of the spilled material. In cases where distance from shore or weather conditions prevent active response (e.g., Argo Merchant, SeaRose platform), this may be the likely response option. In association with this analysis, it is considered the baseline against which other response options may be compared. With natural attenuation, the spilled oil moves with the winds and currents until it eventually evaporates, dissolves, biodegrades, disperses, or strands on the shoreline. Stranded oil will continue to weather and will gradually biodegrade, be incorporated into the sediments, or persist as surface residues. It is possible that some of the relatively fresh oil may be remobilized from where it initially stranded and then transported to other locations before it weathers further, biodegrades, or is deposited permanently. The fate of the oil is generally monitored to determine both if it is attenuating as predicted and if an active response is necessary.

Benefits

Natural attenuation may be appropriate in cases where offshore spills do not threaten shorelines, sensitive habitats, and protected species, or when high sea states exist and natural dispersion is expected to prevail and other response options may not be safely deployed (e.g., during winter months and storm events). In cases where active spill response activities are not appropriate (e.g., when the presence of responders and equipment can damage certain sensitive shoreline habitats), allowing the oil to degrade naturally could be preferable. Additionally, natural attenuation may be necessary in the event that recovery and response are not possible, for whatever reason.

Limitations

By not actively intervening following a spill, there is a likelihood that the public could infer that not enough is being done to respond because there is typically an expectation that everything possible will be done to minimize the spill impact and protect the environment. By its very nature, natural attenuation is a passive tool which will not prevent impacts to high value shoreline habitats if oil were to reach the shore. For offshore slicks, natural attenuation could lead to the presence of oil slicks on the water surface for an extended period of time; for example, hours for light oils during energetic sea states or weeks to months for heavier or emulsified oils during calm sea states. Active monitoring of the area that may be affected by a spill is required because changes in winds and currents may later move the oil into an area where response is necessary. The heavier and emulsified oils that result from natural attenuation are more difficult to respond to if needed. Experience has shown that the recovery of oiled shorelines can range from weeks to months to years, depending on what was spilled and what kind of environmental conditions existed at the time of the spill (e.g., sea state, sunlight intensity, rain, or magnitude of processes contributing to shoreline erosion). Natural attenuation may not be appropriate in situations where it will affect emergency response activities at an offshore platform site, because an active response is more suitable to reducing exposure potentials for surface vessels and personnel to the VOCs of oil and their associated health and safety risks. At a minimum, a conceptual model, followed by a mathematical model, is required for the spill environment and all risk receptors. Monitoring must be done to verify that the model of natural attenuation is proceeding as predicted in regard to these risk receptors. If it is not, then other control methods would be required. If it is meeting the model for natural attenuation, then any requirements for environmental sampling can gradually be relaxed.

Technological Advances

Direct water and sediment sampling for biogeochemistry, remote sensing, and real-time modeling have made advances since the DWH spill. New models of spill fate and effects with and without the use of dispersants (see Chapter 2) can greatly aid *if and when* monitored natural attenuation is applicable.

Effectiveness

Natural attenuation can be an effective option, especially in cases where spilled oil is relatively light and is expected to evaporate/disperse/dissolve relatively quickly; where a spill is not expected to impact sensitive or high value ecosystems; or if extreme weather conditions prevent a safe spill response while also providing the energy required to effectively disperse the oil naturally. Even aggressive remediation techniques should have monitored natural attenuation as the final solution because this will not only save time and resources and will minimize harmful effects of aggressive mediation techniques but also will ensure that the environment and risk receptors are returning to their pre-spill state.

ADDITIONAL CONSIDERATIONS

Dispersant Regulatory Approval Processes

As previously discussed, dispersants represent a potentially significant tool within the spill response toolbox, especially when considering a large-scale, offshore spill scenario. However, while the potential use of dispersants during a response may be technically feasible, regulatory considerations need to be taken into account because they will likely define what products may be used and under what circumstances. To put this in perspective, following the use of solvent-based degreasers during the *Torrey Canyon* spill response in 1967, it was recognized that the use of potentially toxic materials to respond to a spill can make a situation worse. With this in mind, a key aspect of a robust regulatory regime is to have a transparent process of deciding which dispersant products may be used and under what scenario-specific conditions.

In the case of product approval, there are typically two main considerations: the effectiveness of the product and its relative toxicity. Figure 6.3 provides a simple schematic of a product approval process that is used in a number of locations around the world (IPIECA-IOGP, 2014).

In the United States, the U.S. Environmental Protection Agency (EPA) is responsible for managing the process whereby products are listed for possible use. A listing of those products (see Table 6.2) that are available to be considered for use in the event of a spill (i.e., the Product Schedule) is available within Subpart J of the National Oil and Hazardous Substances Pollution Contingency Plan. EPA proposed amendments to Subpart J in 2015 to clarify and update Product Schedule listing procedures. These potential updates included changes to effectiveness and toxicity testing. Public comments were due on or before April 22, 2015. No action has been taken since then.

While products are likely to vary by chemical composition, modern, commercially available dispersants consist of surface active agents (surfactants) and solvents that are generally much less toxic than the materials that may have been used decades ago. During the DWH oil spill response, the Centers for Disease Control released the statement that the "ingredients [of Corexit® 9500A and Corexit® 9527A] are not considered to cause chemical sensitization; the dispersants contain proven, biodegradable and low toxicity surfactants" (CDC, 2010).[1]

A different perspective is provided by the information listed in Table 6.3, which shows the countries in which three particular dispersants have been approved for possible use during a spill response (Carter-Groves, 2014). In particular, following the DWH oil spill, industry established a Global Dispersant Stockpile (GDS) composed of three dispersant products placed strategically in easily accessible locations around the world. The three GDS dispersant products have been studied extensively and are viewed as having some of the broadest global approvals based on effectiveness and toxicity testing.

In the United States, during the response phase of an exercise or spill response, the Incident Command System is used to manage the decision-making process for the use of dispersants or other spill response options, with the Federal On-Scene Coordinator having the lead responsibility. Similar systems are used around the world during emergency responses, sometimes known as the Incident Management System.

By having clear regulatory requirements in place, the decision-making process should be able to proceed in such a manner that the window of opportunity for effective dispersant use is not lost.

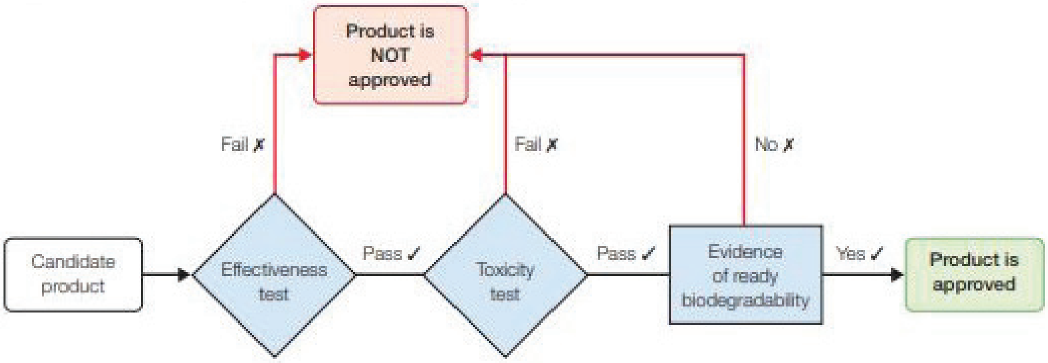


FIGURE 6.3 Example dispersant product approval process. SOURCE: IPIECA-IOGP, 2014.

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[1] See https://www.cdc.gov/nceh/oil_spill/docs/Oil%20Spill%20Dispersant.pdf.

TABLE 6.2 U.S. Environmental Protection Agency National Contingency Plan Listing of Dispersants

ACCELL CLEAN® DWD	JD-2000™
BIODISPERS	MARE CLEAN 200
COREXIT® EC9500A	MARINE D-BLUE CLEAN™
COREXIT® EC9500B	NEOS AB3000
COREXIT® EC9527A	NOKOMIS 3
D SEA BRAT #4	NOKOMIS 3-AA
DISPERSIT SPC 1000TM	SAF-RON GOLD
FFT-SOLUTION®	ZI-400
FINASOL® OSR 52	

SOURCE: EPA; https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100W60V.txt.

TABLE 6.3 National Approvals for Global Dispersant Stockpile Products

Dispersant	Countries of Approval
Dasic Slickgone NS	Australia, Benin, Cyprus, France, Greenland, India, Israel, Libya, Malaysia, New Zealand, Nigeria, Norway, Philippines, ROPME countries (Bahrain, Iran, Iraq, Kuwait, Oman, Qatar, Saudi Arabia, United Arab Emirates), Singapore, Togo, United Kingdom
Finasol OSR 52	Angola, Australia, Benin, Brazil, Cameroon, Congo, Croatia, Cyprus, Egypt, France, India, Indonesia, Israel, Kazakhstan, Malaysia, Morocco, Nigeria, Norway, Philippines, Portugal, ROPME countries (Bahrain, Iran, Iraq, Kuwait, Oman, Qatar, Saudi Arabia, United Arab Emirates), Singapore, Thailand, Togo, United Kingdom, United States, Uruguay
Corexit EC9500A	Angola, Benin, Brazil, Chile, Israel, Libya, New Zealand, ROPME countries (Bahrain, Iran, Iraq, Kuwait, Oman, Qatar, Saudi Arabia, United Arab Emirates), Singapore, Trinidad, United States

NOTE: Correct at the time of publication. SOURCE: Oil Spill Response Limited.

In the absence of clear regulations around their use, discussions about their benefits and limitations may be protracted, especially during the initial reactive stages of an emergency response, and the opportunity to derive environmental benefit could be diminished.

Figure 6.4 highlights the steps that are typically used to determine whether or not an approved dispersant may be applied during a specific spill response scenario (IPIECA-IOGP, 2014).

While a number of countries consider the use of dispersants as either a primary or a secondary response option and have it included in their national contingency plans, it would be beneficial to encourage global consistency with respect to the processes for approving individual dispersant products and allowing for their use (Coolbaugh et al., 2017). As exemplified in Figure 6.5, for approval in Europe, it is likely that there will be significant differences within regions regarding the possible use of dispersants, and this may lead to complications that might hinder an effective response to a spill that could affect more than one country, a topic that will be discussed below.

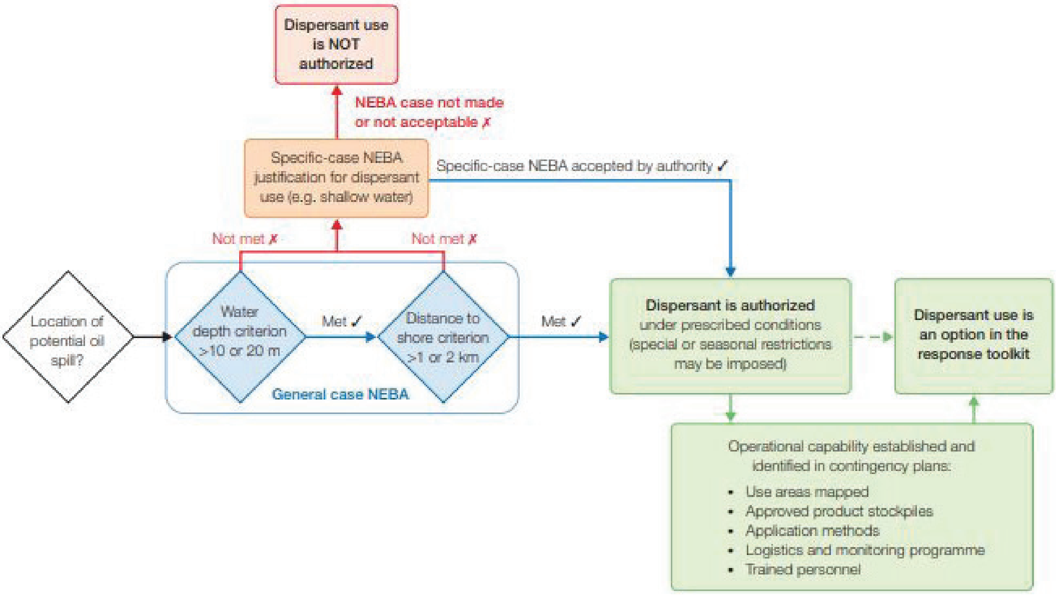

FIGURE 6.4 Example framework for dispersant use approval. SOURCE: IPIECA-IOGP, 2014.

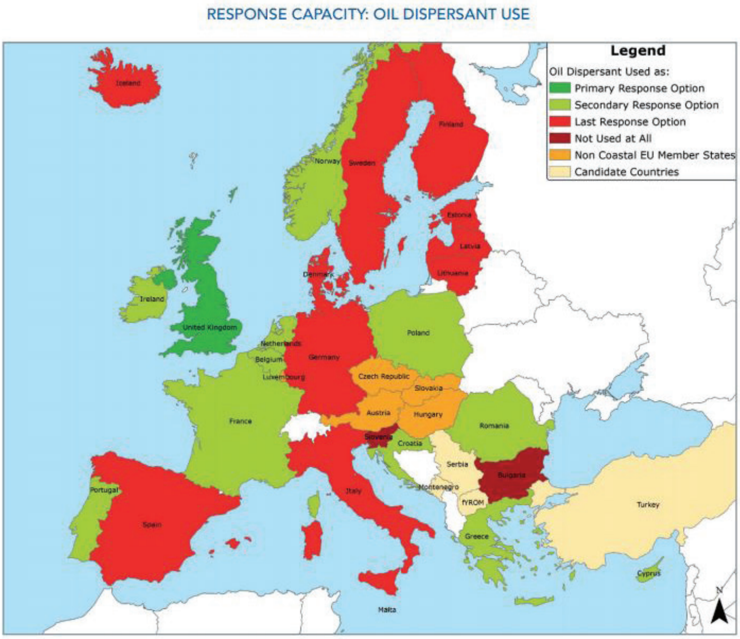

FIGURE 6.5 Dispersant use considerations in Europe. SOURCE: European Maritime Safety Agency, 2014.

Transboundary

It is generally considered that offshore oil spills do not respect international borders. Whether a spill scenario takes place in the Gulf of Mexico, the Strait of Juan de Fuca, or elsewhere in the world, one thing is known: Oil on the water moves over time, and discussions between potentially affected regions should take place before a response is needed. The development of agreements is key, especially when the complexities and potential barriers related to transporting people and equipment across international borders can be a challenge, and especially when time may be of the essence. The return of equipment and personnel in a timely fashion should be considered as well.

A number of international conventions and agreements are currently in existence that help facilitate what might become a transborder spill response. For example, the United Nations Convention on the Law of the Sea (UNCLOS) entered into force in 1982 as a foundational component encouraging international cooperation. Specific articles within the convention focus on preventing, reducing, and controlling marine pollution, and they include the creation of international standards and recommended practices for cooperation as well as defining a process for notifying others who may be affected by a spill. In this respect, UNCLOS has been thought of as the overarching convention that supports others in the actual implementation of various international arrangements, such as the International Maritime Organization (the UN agency responsible for the safety and security of shipping and the prevention of marine pollution by ships) Convention on Oil Pollution Preparedness, Response and Cooperation, which was put into force in 1995 (Chazot and Rhodes, 2017).

Organizations and activities of more regional natures exist and occur, often with an eye toward enhancing cooperation and preparedness across a number of different countries. An example is the Global Initiative program that was created in 1996 following the efforts of the International Maritime Organization and IPIECA to build spill response capacity. Today, Global Initiative programs are present in West Africa, Southeast Asia, and the Black and Caspian Seas region. Other programs have been considered for the wider Caribbean and South America. Through the efforts of these programs, countries that did not have national plans have made major strides. A significant part of the Global Initiative program is to have regular training courses and exercises during which specific focus areas of the member countries can be highlighted and discussed (Coolbaugh et al., 2014). A topic of particular emphasis that has arisen over the past several years is that of transboundary spills and how to respond to them effectively. This is not unique to the Global Initiative regions.

For example, a recent multiyear Mexico–United States (MEXUS) exercise included the possibility of the transboundary movement of oil from U.S. to Mexican waters. Participants from both countries were able to discuss the possible challenges of a transboundary spill and how to address them. For reference, the MEXUS Plan was created following the Ixtoc I well blowout in 1979 in order to facilitate cooperation between the two countries by providing a framework of coordinated operational procedures in case of a spill.

The recent exercise considered such things as specific government agency involvement in customs and border-related issues and various waivers to expedite transfer of equipment and personnel (Drieu et al., 2017).

Arctic

The presence of ice provides additional challenges to oil spill response as it makes reaching the oil more difficult, can foul booms and skimmers, and dampens wave energy. It is also often associated with extreme cold that further inhibits response options. At the same time, these same conditions reduce oil weathering, allowing burning and dispersants to be effective over a longer period than in more temperate waters, and ice can reduce the spreading of oil. How oil and ice interact depend on the type of ice and its concentration (Pegau et al., 2017; Venkatesh et al., 1990).

Another important consideration for oil spill response is that most locations with sea ice are remote, limiting the ability to stage people and equipment, and making the storage and disposal of recovered oil difficult. An important social consideration in the Arctic is that the people have a subsistence lifestyle that is dependent on the marine ecosystem.

Interest in oil and gas development and shipping in the Arctic has led to several reports on oil spill response capabilities and research needs (Bjerkemo, 2013; CRRC, 2017; Dickins, 2004; Holland-Bartels and Pierce, 2011; Lewis and Prince, 2018; NPC, 2015; NRC, 2014; Pew Charitable Trusts, 2013; Pew Environment Group, 2010; Potter et al., 2012; Solsberg, 2008; USARC, 2012; Wilkinson et al., 2017) as well as numerous research projects and programs (e.g., BSEE Arctic Oil Spill Response Research, Oil in Ice Joint Industry Program, and Arctic Response Technology JIP). Lewis and Prince (2018) provide a recent review of dispersant use in the Arctic. The Coastal Response Research Center effort examines in detail what is known about dispersant use in the Arctic. Recent research activities examined remote sensing and advancing response technologies. The use of self-propelled skimmers in ice has been tested, and new skimmers and sorbent materials have been developed. Primary issues with mechanical recovery include the viscosity of the oil; operating booms in an ice environment (although ice can act as a boom); fouling of skimmers by ice; and freezing of skimmer surfaces. Work on in situ burning has focused on the application of chemical herders to thicken the oil to allow a burn (Buist et al., 2008).

In regard to dispersants, some of the recent research with dispersants includes the use of propeller wash as an energy source for mixing (Daling et al., 2010); examining the dispersability of oil frozen in ice (CEDRE, 2016); the fate of dispersed oil under ice (Beegle-Krause et al., 2014); and the effectiveness of dispersants in slush and frazil ice (SL Ross, 2016). Oil frozen in ice was found to be dispersible after 3 months within the ice (CEDRE, 2016). Oil with dispersant frozen in ice was dispersible, but to a limited extent compared to applying fresh dispersants. Fresh oil can be dispersed in frazil ice if mixing energy exists, but the oil weathers and the effectiveness of dispersants declines with time (SL Ross, 2016).

Of particular concern for dispersant use in the ice environment is the issue of reduced mixing energy due to the dampening of wave action by the presence of ice. For dispersants to be effective there must be some mixing energy present. In a broken ice environment, the relative movement of ice provides some mixing energy (Brandvik et al., 2010). The use of propeller wash from a vessel was found to be a viable source of mixing energy (Daling et al., 2010). In many cases, however, mixing energy may be limiting.

UNCERTAINTY IN DECISION-MAKING TOOLS

A comprehensive evaluation of uncertainty in the model estimates described above will be critical for building further acceptance for use in decision making during oil spill response. Formal uncertainty analysis for human health and ecological risk assessment has a rich literature base in its application to decision making associated with implementation of several major environmental acts, including the Clean Air Act, the Clean Water Act, etc. (NRC, 1983, 1994, 2009). Uncertainty can be divided into aleatory (or inherent) uncertainty (also referred to as variability) and epistemic uncertainty (due to limited knowledge of the underlying physical, biological, or chemical processes) (Hoffman and Hammonds, 1994). Aleatory uncertainty can often be incorporated in a straightforward manner; French-McCay et al. (2018b) incorporated the effects of weather variability on oil spill fates using Monte Carlo simulation to find the median case for shoreline and surface impacts. French-McCay and colleagues also incorporated some epistemic uncertainty by looking at two levels of ecotoxicity thresholds. However, in neither case were final results presented that concisely illustrate these uncertainties on the overall risk assessment.

It is also important to note that the modeling by French-McCay et al. (2018b) does not explicitly consider human health risk, although modeled surface VOC levels have been interpreted from a human health perspective (Crowley et al., 2018).

Many federal regulations designed to protect public health are based on application of probabilistic risk assessment (PRA) to estimate the proportion of the human population whose predicted exposures may exceed an established acceptable risk level (as described in Chapter 4 for PAH exposure from fish consumption after an oil spill). Monte Carlo simulation, Bayesian methods, and other approaches are widely used for uncertainty propagation in PRA modeling (Burmaster and Anderson, 1994; Lester et al., 2007). This probabilistic approach can become problematic if exposure to risk levels above the acceptable level, even if estimated at ≤ 1%-5% of the total population, is largely restricted to one specific community. Subsistence fishing communities would be an example of a vulnerable population of concern in oil spill response decision making, as described in Chapter 4.

Given that few studies have specifically assessed ecological and human health effects associated with SSDI, the two hypothetical modeling results shown in Figure 6.6 suggest that uncertainty on the effects of SSDI may be considered too great if panel B were the modeled estimate, but not if panel A were the estimated uncertainty intervals (UIs). In the case of panel B, even if the central probability estimate is less damages with SSDI, under a PRA framework, decision makers may decide it is more important to protect against an even small probability of a higher level of damages, if that damage level crosses a threshold that would be considered unacceptable.

Treatment of uncertainty is largely dependent on first establishing equivalencies in the risk assessments to be compared. For example, CRAs employed to quantify and compare human health risks using the disability-adjusted life year start with the same foundational datasets on life

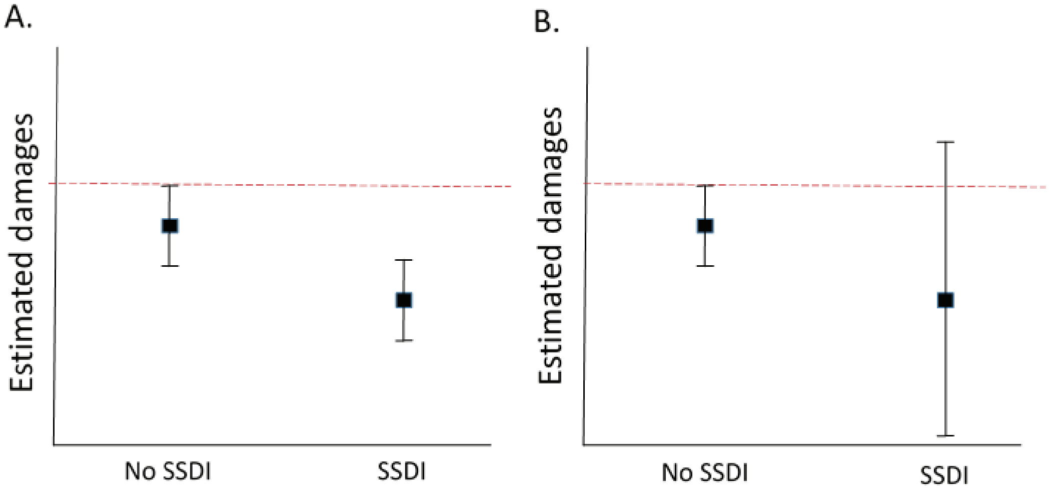

FIGURE 6.6 Hypothetical modeling results of oil spill damage estimates associated with use of subsea dispersant injection (SSDI) versus no SSDI during the response. The uncertainty intervals represent propagation of both aleatory and epistemic uncertainty in model. The dashed red line represents a threshold of damages deemed unacceptable by decision makers. NOTE: This is a fictitious and unitless example.

expectancy and disease states to minimize differences in the treatment of aleatory uncertainty, and consider sources of epistemic uncertainty in exposure and exposure-risk relationships in a consistent manner (Danaei et al., 2005). UIs are estimated not only using quantitative empirical data; often they will incorporate qualitative data (expert judgment) to address epistemic uncertainty and build probability distributions for parameters when empirical data are limited (Budnitz et al., 1998; Morgan, 2014; Rabl and Spadaro, 1999). This human health application of CRA has subsequently been incorporated into life cycle analyses and external cost models assessing and comparing human health, ecological, and natural resource damages across different systems for electricity generation or nuclear weapons stockpiling, for example (Helton, 2011; Huijbregts et al., 2017; Jolliet et al., 2003; Krewitt, 2002; NRC, 2009).

As models are being developed to describe more complex systems, clear and transparent methods for treatment of both types of uncertainty will be useful for informed decision making. In some cases, a comprehensive qualitative assessment of uncertainty communicated to decision makers may be more practical given time and resource constraints, and absence of quantitative uncertainty analysis should not be used as grounds for inaction (Goldstein, 2011).

COMPARISON STUDIES OF RESPONSE METHODS

As discussed in the previous chapter and highlighted in Figure 5.3, there is considerable complexity in being able to understand how decisions about response options may impact environmental and human health. The complexity of the potential environmental impacts, along with few real-world opportunities for scientific studies of spilled oil, has limited direct observations of the trade-offs associated with decisions about dispersant application. One notable exception is the Tropical Oil Pollution Investigations in Coastal Systems (TROPICS) experiment.

Tropical Oil Pollution Investigations in Coastal Systems

A well-documented Net Environmental Benefit Analysis (NEBA)-based dispersant effects study was undertaken in Panama starting in 1983. The TROPICS study established three study sites in order to evaluate the short- and long-term effects of undispersed and dispersed oil (along with a control site) on an ecosystem that included shallow-water coral, sea grass, and intertidal mangroves (Baca et al., 2014; see Figure 6.7). Periodically, the sites were visited, and the relative health of the sites was evaluated over a 32-year period. The most recent visit was in 2015 (Renegar et al., 2017b).

During the first phase of the study, results showed that in the first 10 years, the plot exposed to dispersed oil had recovered to pre-spill conditions, while the site that experienced undispersed oil still showed negative effects to the affected mangroves. In the ensuing years, the sites continued to display differences in recovery, and there is a clear demonstration that exposure to dispersed oil was less disruptive overall to the marine and intertidal communities.

While the water column species were exposed to higher levels of hydrocarbon during the initial and relatively severe conditions of the experiment, long-term health of the ecosystem was more affected by the impacts to the mangroves, and a neutral comparison of the ecosystem components would favor a decision to use dispersants. In different scenarios, it is entirely possible that other weighting factors defined by regional priorities could come into play that change the outcome of a NEBA, but in this case, the observations from the TROPICS study are focused only on the relative health of the ecosystem and do not encompass broader socioeconomic, human health, or other considerations that could be part of a Spill Impact Mitigation Assessment (SIMA) evaluation.

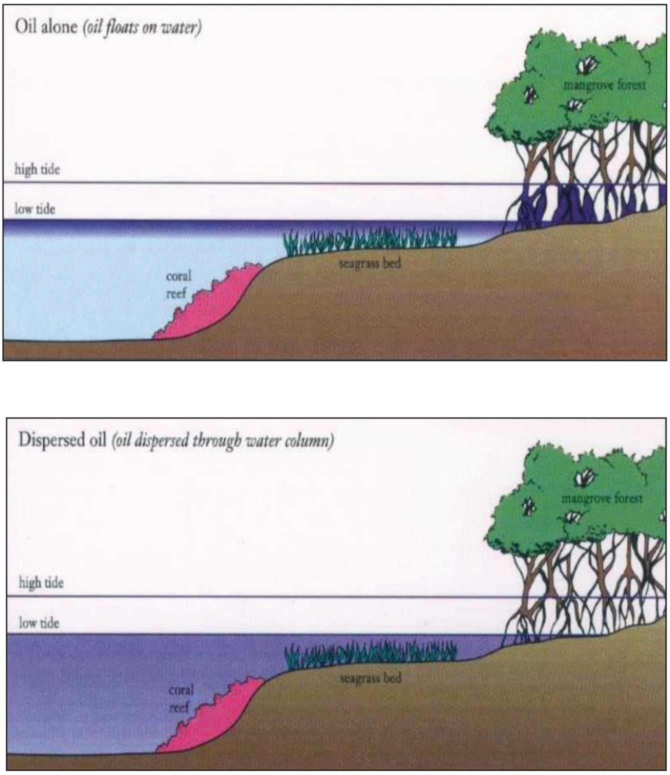

FIGURE 6.7 TROPICS created two exposure scenarios in marine tropical ecosystem habitats: Top, non-dispersed oil (Site O) and Bottom, dispersed oil (Site D). SOURCE: Baca et al., 2014.

CRA SSDI Studies

Recent advances in numerical modeling have allowed the examination of the potential impacts of the application of dispersants and other response options through the use of the CRA tool. Numerical models that integrate all the different processes described in this report have allowed evaluations of environmental and human health impacts that may arise from different decisions in a response.

The first CRA of responses to a deepwater blowout is described in Bock et al. (2018), French-McCay et al. (2018a), and Walker et al. (2018a), and was funded by the American Petroleum Institute (API). We will refer to this study as “CRA-1” to differentiate it from the generic term “CRA” used to describe this general class of tool first introduced in Chapter 5, as well as from the CRA-2 study that extended the CRA-1 to other sites.

Before reviewing these studies, it is important for the reader to note two important characteristics of CRAs:

1. Site specific. That means it can be difficult to extend what is learned at the CRA site to another site because of differing key physical factors, such as water depth, distance to shore, and atmospheric/ocean climatology, as well as differing key biological factors, such as habitat and species distribution.

2. Model dependent. CRAs rely almost totally on integrated models. This removes subjectivity from the risk assessment of a SIMA or a Consensus Ecological Risk Assessment, but as indicated in Chapter 5, integrated models are imperfect. While many of the models are well validated at a process level, they are not well validated at the "integrated" level. In the case of the CRA-1, the integrated model has been validated to some degree with the DWH observations (Spaulding et al., 2017), but the risk assessments resulting from the CRA-1 have not been. That said, when an integrated model is used to compare various response options, many model uncertainties may tend to cancel each other, making the relative prediction more accurate than an absolute prediction.

CRA-1 Study Description

CRA-1 considered a single site with DWH-like oil flowing at 45 kb/d located in the northeastern Gulf of Mexico in 1,400 m of water about 222 km from the nearest coast (three times further offshore than DWH). The spill was capped at 21 days and SSDI started after day 6.

Figure 6.8 shows a schematic of the methodology. The 4-D (x, y, z, t) concentration fields of 19 hydrocarbon constituents were calculated using RPS ASA's OILMAP DEEP in the nearfield and SIMAP in the farfield fate (see Table 5.1 for a summary of these models). To account for natural weather variability, 100 trajectory-only model runs were made using weather and current time series whose start date was randomly selected from regional models covering 5 years. From these 100 runs, a statistically rare event was chosen which ranked roughly in the 95th percentile in terms of

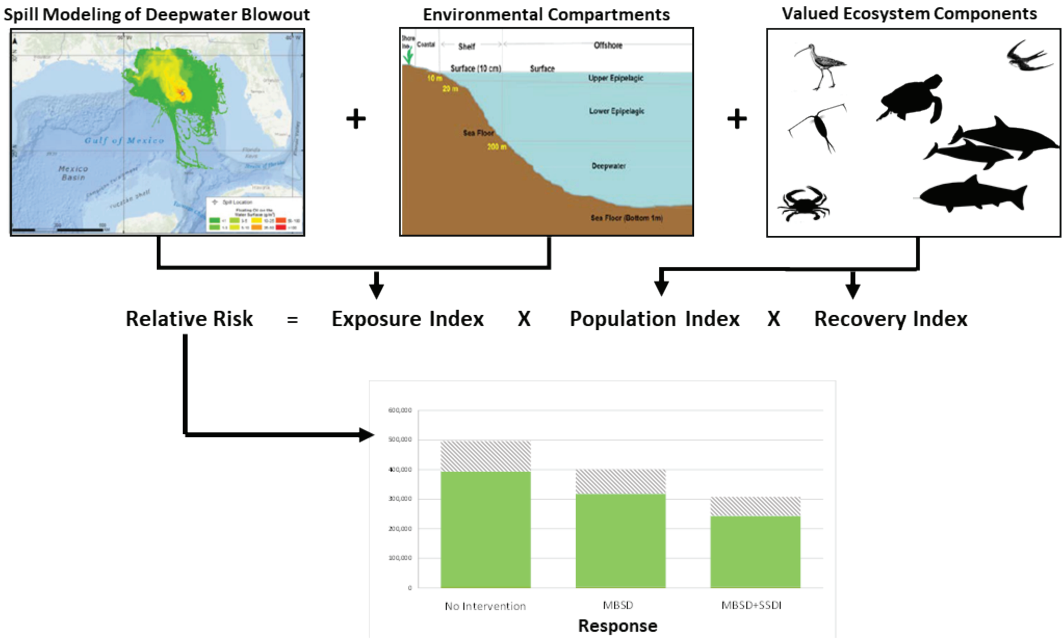

FIGURE 6.8 Schematic showing major steps in the CRA-1 (Bock et al., 2018). The first step is to calculate the 4-D fields of concentrations for the hydrocarbon constituents using a spill model. The second and third steps use resource maps to identify spatial distribution (environmental compartments [ECs]) of important biota (valued ecosystem components [VECs]). The relative risk is then calculated as the exposure of each VEC times the VEC density in each EC times the recovery rate for each VEC. SOURCE: Bock et al., 2018.

total oiled surface area and shoreline (5 of the 100 runs caused heavier oiling).[2] This weather-current configuration was then used as the basis for further runs that compared oil mass distributions and ecological impact assuming four response options: no response, traditional responses (mechanical, burning, and surface dispersants), mechanical only, and SSDI plus traditional responses.

The ecological impacts of the blowout were estimated by calculating the exposure to hydrocarbon of valued ecosystem components (VECs) distributed geographically through environmental compartments (ECs). A total of 12 VECs, representing important species, were considered (e.g., zooplankton, birds, turtles, soft bottom macrobenthos) distributed through 13 ECs. In the vertical dimension, the ECs were segmented into seven levels (e.g., surface, lower epipelagic, etc.). In the horizontal cross-shelf dimension they were broken into four regions (shore, nearshore, shelf, and offshore).

Exposure scores were developed for each VEC in each EC. Toxic thresholds were derived from various sources, including the Natural Resource Damage Assessment (NRDA) for the DWH spill. Because these thresholds are highly uncertain, two thresholds were investigated: a lower (upper) toxicity threshold case is referred to as the low (high) threshold.

Once the exposure scores were determined for each VEC in each EC, further computations were performed to combine the exposure with the population density and species recovery time into a single number normalized by the maximum possible for the VEC in that EC (see equation in Figure 6.8). This “Relative Risk” varied from 0 to 1 with 0 meaning that there was no risk (exposure) and 1 indicating the maximum possible relative risk (i.e., the entire population was exposed to concentrations above the threshold during the entire simulation in the VEC with the longest recovery time).

CRA-1 Key Results

For this particular scenario, the CRA-1 study found:

1. Mechanical and burning removed a small fraction (a few percent) of the oil. Surface dispersant removed significantly more but still less than about 15% at the time that surface oil peaked. In contrast, SSDI substantially reduced surfacing oil (~50%) and shoreline oil (~70%) more than any of the other responses did. However, SSDI substantially increased the volume of hydrocarbons in the water column, most of it at the plume trapping depth located at roughly 300 m above the seafloor.
2. The “no-intervention case” always had the highest damage scores regardless of the toxicity threshold. In other words, some response was always better than no response. Traditional response (mechanical, burn, surface dispersant) reduced the no-intervention damage score by about 20% regardless of the assumed exposure thresholds.
3. SSDI alone reduced the no-intervention damage score by 20% when a low toxicity threshold was assumed, but it decreased it by 40% for the high toxicity thresholds. In other words, SSDI was always at least as good as all other responses combined.
4. The VECs that suffered the most damage depended on the assumed toxicity threshold. For the high threshold, birds dominated the damage score, while for the low threshold, turtles and mammals dominated. The ECs that suffered the most damage also depended on the assumed toxicity threshold. For the high thresholds, shoreline damage contributed most. For the low thresholds, the sea surface on the shelf and in deep water dominated.

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[2] A case that was near the median (50%) was also identified and studied, but because all the oil stayed far from shore, there was little nearshore impact under any response scenario.

The key take-away from CRA-1 is that SSDI significantly reduced the damage for the majority of the species (VECs) in the majority of the ECs. Surface species benefited most from the use of SSDI, while species at depth in deep water saw only a slight increase in damage. However, the reader is reminded of several caveats. First, these results make a number of assumptions which can be legitimately questioned; for example, few species are tracked and the interaction between species is not considered. Second, the CRA results have not been validated in any way by comparing them with observed damages. Finally, the results may change substantially if the scenario were to change.

Extension (CRA-2) Project Description

CRA-2 (French-McCay et al., 2018b) is an extension of CRA-1 intended to explore the sensitivity of the fates to changes in flow rate and blowout location (e.g., distance from shore and water depth). Two sites were considered in the north central Gulf of Mexico not far from the Macondo well. The shallower site was in 500 m and the deeper site in 1,400 m. The same oil and methods were used as French-McCay et al. (2018a) except (a) only the fates models (no effects) were run because of budget constraints, and (b) the median (50% non-exceedance) weather-current stochastic run was used instead of the 95% non-exceedance. Less oil reaches shore in the 50% case than in the 95% case, so this case will show fewer benefits of SSDI than a 95% case will, all else being equal. That said, the 50% case is much more likely to be realized than is the 95% case.

The CRA-2 plotted most results in terms of the droplet size to emphasize the importance of that parameter and to avoid tying results to a single droplet model. The droplet size can be related to a flow rate using one of the droplet models described in Chapter 2.

CRA-2 Key Results

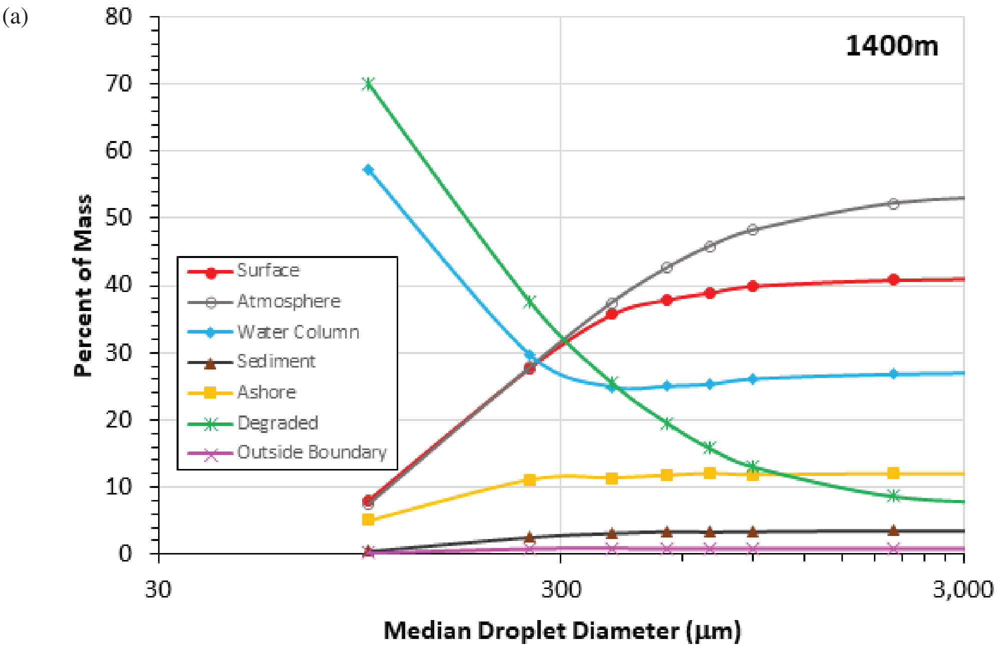
Summarizing the results of a CRA-type study is challenging because model output is voluminous, and no single metric captures all the possible impacts of SSDI. One of the more revealing metrics is shown in Figure 6.9, which displays the peak mass distributed in the indicated environmental compartment (e.g., surface, ashore, etc.) at any time in the 66 days. These will not add up to 100% because each point on a curve is the peak for that component at any time. For compartments where oil accumulates over the course of the 66 days (sediment, ashore, degradation, and atmosphere), the curves will also represent the final mass distribution. In the subsequent discussion we will use the term “fates benefits” as shorthand to signify beneficial changes in the various environmental compartments. Such changes would include reductions in oil reaching the surface, seafloor, and atmosphere, or increases in degradation. A “cost” would be an increase in subsurface oil.

Figure 6.9 shows that the fates benefits of small droplets start to accrue when the median droplet size (d_{50}) drops below about 1 mm in 1,400 m, while in 500 m of water benefits do not appear until about 300 μm. The discussion below will refer to these d_{50}s as the “cutoff size.”

It should be noted that there are some fates benefits that are not captured in Figure 6.9. Probably the most important one is that the location of the surfacing oil will tend to shift downstream of the well when SSDI is used. That is because SSDI will generate smaller droplets than without. While these droplets may still be fairly large and rise to the surface quickly, the fact remains they will take longer to rise than without SSDI. This means that unless the currents are totally slack, some of the surfacing oil will be pushed by the prevailing currents further downstream of the well thus reducing the VOCs in the vicinity of high human activity. Unfortunately, neither the CRA-1 nor the CRA-2 provided metrics that quantify this benefit.

Figure 6.9 reveals that decreasing the droplet size can substantially increase fates benefits. For example, in 1,400 m, if the d_{50} is decreased by an order of magnitude from 3,000 to 300 μm, the

(a)



(b)

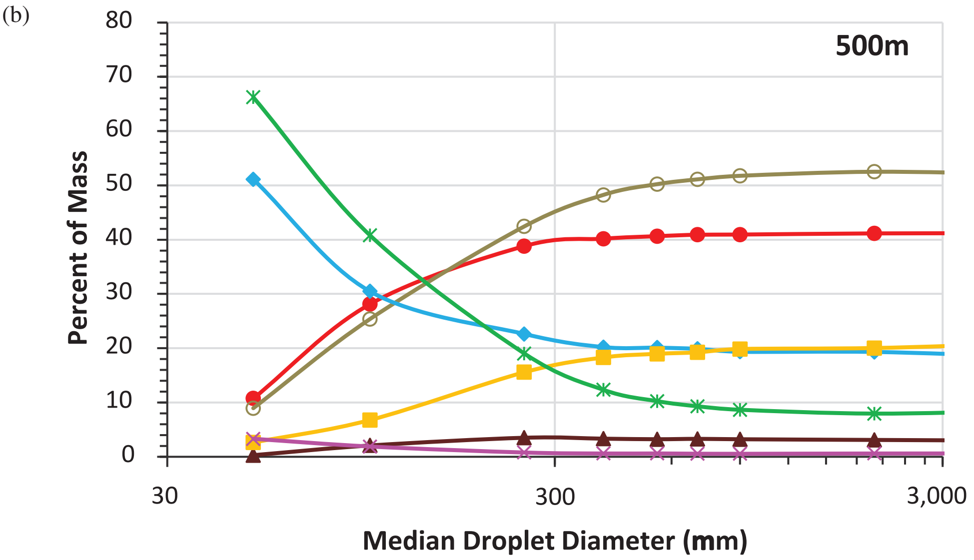


FIGURE 6.9 Peak mass distribution (as a percentage of the total mass discharged) at **any time** during the 66-day simulation versus droplet size for the Extended CRA runs (French-McCay et al., 2018b). Upper (lower) figure is for a 1,400 m (500 m) site. Note one cannot add up the percentage mass for the curves and expect them to be 100% because each point on a curve is the peak for that component at any time. SOURCE: Adapted from French-McCay et al., 2018b.

peak surface mass drops from 40% to 30% of the total, degradation is increased from less than 10% to more than 30%, and evaporation (atmosphere) is reduced from 50% to 30%. In the case of degradation and evaporation, these reductions apply to the final mass distribution as well as the peak mass. All the benefits identified above come at little cost because the mass in the water column remains stable. One sees similar behavior in the curves at 500 m, though as noted earlier, benefits start at a much lower cutoff size of 300 μm. The figure for 1,400 m also shows that as the d_{50} drops below 300 μm, most of the potential benefits accelerate rapidly. Most notable is the drop in the length of shoreline coated by oil. This highly nonlinear behavior means that there can be big benefits in driving the droplet size well below the cutoff size.

All the fates benefits outlined above can come at a cost in the form of an increase in the peak mass in the water column (blue curve in Figure 6.9). It is a cost because it means subsurface biota will be exposed to more oil. However, a detailed look at concentrations in the subsurface would likely show only modest increases because the hydrocarbon is being added to a thick (order 100 m), deep (200-400 m above bottom) intrusion layer being dispersed in three-dimensions.

Figure 6.9 shows that degradation plays a big role when the droplets fall below the cutoff size. Degradation does not include evaporation (this is included in the "atmosphere" compartment) but does include biodegradation and photooxidation of PAHs in the upper water column. Most of the biodegradation results from dissolution of aromatic hydrocarbons (French-McCay et al., 2018a).

As pointed out above, the fates benefits of SSDI at 500 m do not start until the d_{50} drops below the critical size of 300 μm, roughly one-third that in 1,400 m. This makes sense because many of the droplets heading to the surface travel a much shorter distance in 500 m, thus allowing for less degradation and dilution. It might be tempting to conclude that SSDI is more beneficial in deeper water than in shallow water, but the presence of gas in a blowout complicates the situation. When in 500 m, the gas is less compressed then in 1,400 m and so the exit velocity will be higher and the droplet size smaller (Johansen et al., 2013) with or without SSDI. French-McCay et al. (2018b) explored this issue by looking at 28 blowout scenarios in their Table 2. Figure 6.10 below summarizes some of those results for two water depths with 1:100 DOR[3] and two gas-to-oil ratios (GORs) (500 and 2,000). The gradated blue rectangular areas denote the flow rates where net fates benefits will result: that is, the d_{50} is less than the critical droplet size for that water depth. It is readily apparent that in 1,400 m, SSDI provides net benefits for almost any flow rate, while in 500 m the flow rate must be larger, especially for lower GORs. For example, at a GOR = 500, the figure shows that for flow rates less than about 40 kbbl/day there would be no fates benefits.[4] One sees a similar, though less pronounced, trend at a GOR = 2,000: for example, in 500 m, there are few benefits for flows less than 20 kbbl/day, while in 1,400 m this limit is 10 kbbl/day. In summary, SSDI will generally have fewer fates benefits at the 500 m site than at the 1,400 m site, all else being equal; and, at some threshold water depth, SSDI benefits will become negligible.

The CRA-2 study did not calculate the "effects" benefits which could be an interesting additional effort, as would the use of toxic units in place of concentration thresholds.

Comparative VOC Study

Crowley et al. (2018) studied the effect of SSDI on near-surface atmospheric VOCs emitted near the well during a DWH-like blowout using the RPS ASA integrated oil-fates model for the ocean and a numerical model for the atmosphere (SCIPUFF). The inputs such as the oil type and

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[3] A GOR of 1:100 was chosen because it is near the optimal value for the light oils that will characterize larger blowouts (Brandvik et al., 2013, 2014a,b): for instance, an increase in GOR to 1:50 only reduces droplet size about a further 20%.

[4] Recall from the earlier discussion that the CRA-2 did not quantify the benefits that might result moving the surfacing oil slick further downstream of the work area. If this benefit were somehow quantified it might prove substantial enough to change the conclusion in this sentence.

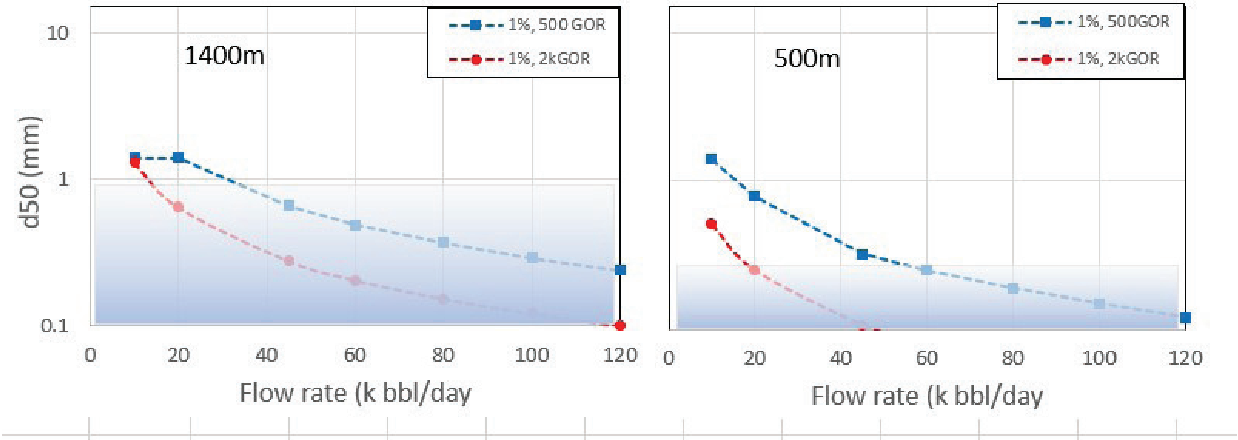


FIGURE 6.10 The median droplet size (d_{50}) versus flow rate for two water depths (1,400 m on the left, 500 m on the right) and two GORs (500 and 2,000). SSDI = 1:100. Results plotted from Table 2 of French-McCay et al. (2018b). The gradated background serves as a reminder that fates benefits rapidly increase as the droplet size decreases beneath the critical droplet size. SOURCE: Data from French-McCay et al., 2018b.

site location were identical to the CRA-1 study (French-McCay, 2018a). While Crowley et al. (2018) only looked at the case with no response and the case with SSDI, it can be argued that VOCs near the well with no response will look similar to the VOCs with traditional response. That is because none of the traditional response methods are allowed to get close to the well site for safety reasons, and hence are unable to remove any surfacing oil near the well which is the primary source of VOCs near the well.

Wind speed and direction play a key role in controlling VOC concentrations so a stochastic wind modeling step was first performed to determine three distinct wind events that would cause low, medium, and high VOC concentrations within a 1-week period. Currents are also a stochastic process that can affect the volume and location of the surfacing oil which in turn can affect VOC concentrations near the well. Because currents and winds are not well correlated in deep water, accounting for their joint statistics means many different combinations must be considered. To avoid this complexity, the study assumed a current profile based on an average for the site.

The actual simulation began by running the integrated fates model without SSDI and with 1% (1:100) SSDI. The result was a three-dimensional field (x, y, and t) of volatilized VOC flux in the vicinity of the well with and without SSDI on a 20 km square grid with 1 km resolution centered on the well.

The surface VOC fluxes were then fed into the atmospheric model for the three wind cases yielding six total cases (three wind cases times the two SSDI cases). The atmospheric model used a 20 km square grid with 100 m resolution centered on the well. Results were saved at 0, 1, 10, and 100 m above the sea surface.

The study concludes that SSDI reduces peak VOCs by factors of 100-200 times depending on the wind condition.

A key question is this: Do the concentrations found by Crowley et al. (2018) without SSDI represent a significant threat to worker health and safety? According to Crowley et al. (2018) the answer is not easily obtained. The problem stems from the fact that agencies involved in worker safety typically set standards based on a time average of 8 to 12 hours. In an actual spill response, safety personnel will typically shut down operations if concentrations exceed those 8- to 12-hour thresholds for only minutes. With that in mind, Crowley et al. (2018) interviewed several industrial hygienists involved in spill response who suggested an instantaneous limit of about 25 ppm for total VOCs. Crowley found that without SSDI, VOCs exceeded this threshold many times. One obvious problem with the Crowley work is that there is no model validation.

Model of Gros et al. (2017)

Description of Original Effort

Gros et al. (2017) applied the Texas A&M Oilspill Calculator (TAMOC) model summarized in Table 5.1 to evaluate the effectiveness of SSDI during the DWH spill. To validate the model, they compared results to observed concentrations of many oil constituents (e.g., benzene, toluene, etc.) measured in the intrusion layer (900-1,300 m depth) and in the atmosphere. They found good agreement using a 0.4% (1:250) DOR (best estimate of the dispersant dosage during this day). Once the model was validated, they used it to estimate the distribution of oil through the water column during DWH. They then ran the model using no dispersant. Their important findings were:

1. 24% of the hydrocarbon ended up in the intrusion layer, mostly as aqueously dissolved compounds and 0.8% as microdroplets.
2. Dispersant was estimated to decrease the median droplet size by a factor of three and increase hydrocarbon dissolution by 25%.

3. Dispersant increased the volume of soluble hydrocarbon retained in the lower water column by 55% and reduced the volume of oil that surfaced, reducing the VOCs in the atmosphere by 28%.

The dispersant effectiveness suggested by the model is substantial and notable in that it was achieved with what was almost certainly a suboptimal dosage of 0.4% (1:250) DOR. Work by Brandvik et al. (2013, 2014a) on Macondo-like oil has shown that a DOR of 1:100 to 1:50 is probably optimal for a subsurface oil spill and would result in a droplet reduction of three times more than that observed with a DOR of 1:250.

Description of Additional Runs

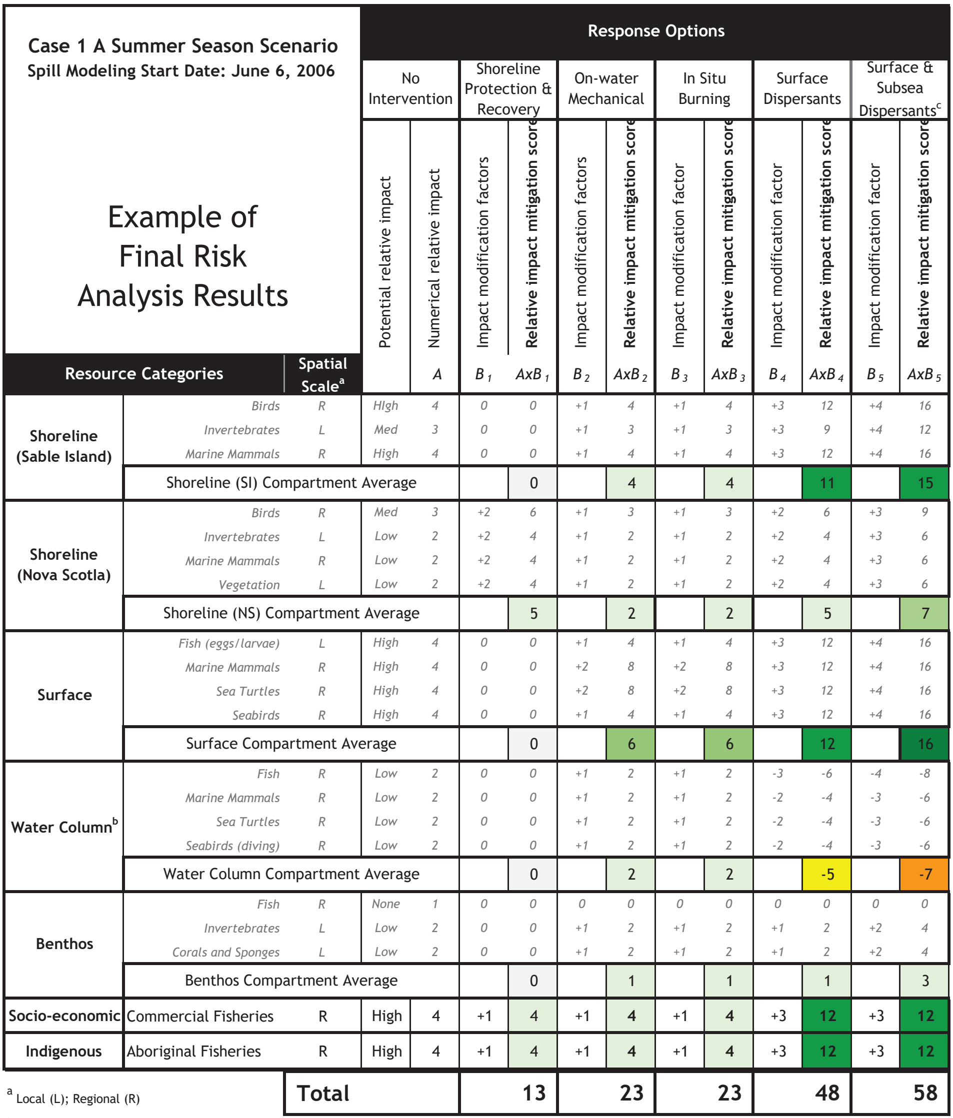
To further investigate the sensitivity of the Gros et al. (2017) results to changes in DOR and droplet size model, the committee commissioned Socolofsky and Gros to make four additional runs using different DSDs. The additional model runs are described in more detail in Appendix E. The most important findings were as follows:

1. If the DOR during DWH had been increased from 1:250 to a more optimal 1:100 this would have eliminated virtually all the oil from surfacing. The committee interprets this to suggest that VOCs and shoreline oiling would likely be negligible.
2. The comparisons with the Gros et al. (2017) DWH dataset suggest that the d_{50} during DWH was about 1 mm. Both the VDROP-J and the SINTEF model give values near this assuming a DOR of 1:250 (the average DOR during this time period suggested by Gros et al., 2017).
3. The RPS ASA's DSD used for the DWH NRDA (Spaulding et al., 2017) does not reproduce critical characteristics of the Gros et al. (2017) dataset. In general, the NRDA DSD overestimates the oil in the intrusion layer. It also overestimates the lighter factions making it to the surface thus suggesting that one could not simply adjust RPS ASA's assumed mixing efficiency.
4. The smallest droplet size tested (115 µm) overestimates most of the oil components in the intrusion layer by factors of two to three times, while at the surface there is virtually no oil except for a few higher end components, which are still underestimated by factors of more than two times. By analogy, the 70 µm droplet size used by Paris et al. (2012) DSD would have even larger discrepancies. One sees opposite trends of similar magnitude if the d_{50} = 10 mm.

Spill Impact Mitigation Assessment of Subsea Dispersant Injection

In 2017, a SIMA was prepared for the Scotian Basin exploration drilling project initiated by BP Canada Energy Group focused on an offshore source control event in Nova Scotia (Slaughter et al., 2017). As can be seen in the example SIMA output below (see Figure 6.11; see Chapter 5 for the methodology), the end result is one that can help frame the discussion about the mitigating aspects of each spill response tool in relation to the potential ecosystem impacts.

The framework for identifying resources of concern (ROCs) for this SIMA consisted of understanding ecosystem health, human safety, and socioeconomic concerns in a given area (e.g., platform location, pipeline route, shipping channel, etc.). Key resources were identified using physical, biological, and socioeconomic data for the region, and they were also pulled from existing studies for that region (e.g., Environmental Impact Statements, seismic surveys, and biological assessments).



Case 1 A Summer Season Scenario
Spill Modeling Start Date: June 6, 2006

Example of
Final Risk
Analysis Results

Resource Categories		Spatial Scale[a]			Response Options									
			No Intervention		Shoreline Protection & Recovery		On-water Mechanical		In Situ Burning		Surface Dispersants		Surface & Subsea Dispersants[c]	
			Potential relative impact	Numerical relative impact	Impact modification factors	**Relative impact mitigation score**	Impact modification factors	**Relative impact mitigation score**	Impact modification factor	**Relative impact mitigation score**	Impact modification factor	**Relative impact mitigation score**	Impact modification factor	**Relative impact mitigation score**
				A	B_1	AxB_1	B_2	AxB_2	B_3	AxB_3	B_4	AxB_4	B_5	AxB_5
Shoreline (Sable Island)	Birds	R	HIgh	4	0	0	+1	4	+1	4	+3	12	+4	16
	Invertebrates	L	Med	3	0	0	+1	3	+1	3	+3	9	+4	12
	Marine Mammals	R	High	4	0	0	+1	4	+1	4	+3	12	+4	16
	Shoreline (SI) Compartment Average					0		4		4		11		15
Shoreline (Nova Scotla)	Birds	R	Med	3	+2	6	+1	3	+1	3	+2	6	+3	9
	Invertebrates	L	Low	2	+2	4	+1	2	+1	2	+2	4	+3	6
	Marine Mammals	R	Low	2	+2	4	+1	2	+1	2	+2	4	+3	6
	Vegetation	L	Low	2	+2	4	+1	2	+1	2	+2	4	+3	6
	Shoreline (NS) Compartment Average					5		2		2		5		7
Surface	Fish (eggs/larvae)	L	High	4	0	0	+1	4	+1	4	+3	12	+4	16
	Marine Mammals	R	High	4	0	0	+2	8	+2	8	+3	12	+4	16
	Sea Turtles	R	High	4	0	0	+2	8	+2	8	+3	12	+4	16
	Seabirds	R	High	4	0	0	+1	4	+1	4	+3	12	+4	16
	Surface Compartment Average					0		6		6		12		16
Water Column[b]	Fish	R	Low	2	0	0	+1	2	+1	2	-3	-6	-4	-8
	Marine Mammals	R	Low	2	0	0	+1	2	+1	2	-2	-4	-3	-6
	Sea Turtles	R	Low	2	0	0	+1	2	+1	2	-2	-4	-3	-6
	Seabirds (diving)	R	Low	2	0	0	+1	2	+1	2	-2	-4	-3	-6
	Water Column Compartment Average					0		2		2		-5		-7
Benthos	Fish	R	None	1	0	0	0	0	0	0	0	0	0	0
	Invertebrates	L	Low	2	0	0	+1	2	+1	2	+1	2	+2	4
	Corals and Sponges	L	Low	2	0	0	+1	2	+1	2	+1	2	+2	4
	Benthos Compartment Average					0		1		1		1		3
Socio-economic	Commercial Fisheries	R	High	4	+1	4	+1	4	+1	4	+3	12	+3	12
Indigenous	Aboriginal Fisheries	R	High	4	+1	4	+1	4	+1	4	+3	12	+3	12
			Total			**13**		**23**		**23**		**48**		**58**

[a] Local (L); Regional (R)

[b]Based on the top 100 m of the water column, as described in the modeling results.

[c]Surface dispersant only for days 2-9; surface and subsea dispersants for days 10-30.

FIGURE 6.11 Representative output of a SIMA evaluation. SOURCE: Modified from Sponson Group, 2017.

TABLE 6.4 Example Resources of Concern Table Used to Support the SIMA Process

Area	Habitat	Habitat	Resource Category
Shoreline	Nova Scotia Intertidal	Marine intertidal zone is defined as the area of the foreshore and seabed that is exposed to the air at low tide and submerged at high tide.	Birds Invertebrates Mammals Vegetation
	Sable Island Intertidal	Marine intertidal zone is defined as the area of the foreshore and seabed that is exposed to the air at low tide and submerged at high tide.	Birds Invertebrates Mammals Vegetation
	Cultural and Subsistence		
Shelf (from subtidal zone to the shelf break)	Sea Surface	The sea surface microlayer (SML) is the top 1 millimeter of the ocean surface. This is the boundary layer where exchanges occur between the atmosphere and the ocean surface.	Birds Marine Mammals Fish eggs/larvae Sea Turtles
	Water Column *(shallow: less than 20m)*	The oceanic mixed layer pelagic environment from the surface to the depth of ~20 m.	Birds (Diving) Fish eggs/larvae Fish Marine Mammals Plankton Sea Turtles Vegetation
	Water Column *(deeper: greater than 20 m)*	The marine pelagic environment from the oceanic mixed layer (~20 m) to the boundary of the benthic zone.	Birds (Diving) Fish Fish eggs/larvae Plankton Marine Mammals Sea Turtles
	Benthos	The benthic zone is the lowest level in the marine environment which includes the sediment surface as well as subsurface layers.	Corals and Sponges Fish eggs/larvae Invertebrates Fish

continued

TABLE 6.4 Continued

Area	Habitat	Habitat	Resource Category
Slope (extending offshore from the shelf break)	Sea Surface	The SML is the top 1 millimeter of the ocean surface. This is the boundary layer where exchanges occur between the atmosphere and the ocean surface.	Birds Marine Mammals Fish eggs/larvae Sea Turtles
	Water Column *(shallow: less than 20 m)*	The oceanic mixed layer pelagic environment from the surface to the depth of ~20 m.	Birds (Diving) Fish eggs/larvae Fish Marine Mammals Plankton Sea Turtles
	Water Column *(deep: greater than 20 m)*	The marine pelagic environment from the oceanic mixed layer (~20 m) to the boundary of the benthic zone.	Birds (diving) Fish Marine Mammals Fish eggs/larvae Invertebrates Plankton Sea Turtles
	Benthos	The benthic zone is the lowest level in the marine environment that includes the sediment surface as well as subsurface layers.	Corals and Sponges Invertebrates Fish
Socioeconomic	Commercial Fisheries Indigenous Fisheries Marine Transportation Tourism/Recreation Oil and Gas Operations Research Activities Aquaculture		

SOURCE: Modified from Sponson Group, 2017.

In addition, key resources were identified via engagement with various federal, regional, and local regulators, aboriginal organizations, fish producers and fish associations, nongovernmental stakeholders, and the public (during development of the lease block Environmental Impact Statement). These efforts helped build positive relationships and trust, and they provided transparent and timely communication about perceived risks of oil spills in that area. The engagement process also provided a forum for understanding stakeholders' priorities, which are taken into consideration and incorporated in the SIMA's ROCs.

In addition to information that pulled from the Environmental Impact Statements and other regional assessments, the fate and behavior of oil in the spill scenario were studied to identify resources that may be distinctively affected due to age, species type, sensitivity to oil, etc. These resources are taken into consideration during the risk assessment phase of the SIMA.

A geographical area, a habitat, and a representative species list for each ROC was summarized in a table to aid in the SIMA. The representative species is a suitable example of a species, resource category, or other valued component for the region. The representatives may include species designated as threatened or endangered or otherwise protected under that government's environmental policies.

Under the framework described above, the following resources were identified as ROCs: migratory birds, fish, invertebrates, marine mammals, sea turtles, marine plants, corals and sponges, commercial fisheries, recreational fisheries, cultural and subsistence uses, special areas (marine transportation, military uses, drinking water intakes), and protected areas.

An example of a ROC table (see Table 6.4) is provided to emphasize the difference between habitats that are offshore, on the slope, on the shelf, and on the shoreline. The assessment considers the generalized ecological communities or habitat types that exist in the affected area, except in instances where a particular species or community is integral to the evaluation.

In addition to ecological resources, this table includes socioeconomic and safety resources because a high level of importance is attached to them. These resources are depicted crossing both the habitat and the resource category column in the table to symbolize their assignment across all resource categories and habitats. In particular, commercial fisheries is an important resource for most governments, so it should therefore be included as a ROC. In addition, cultural and subsistence (aka "aboriginal use") for both historic fisheries and commercial fisheries can be included as a ROC. Other socioeconomic factors such as marine traffic, military use of the waters, recreational boating, and scuba diving could also be added to the ROC table. As shown in Figure 6.11, there were both positive and negative impacts potentially associated with surface or subsea dispersant use, with the balance being favorable for their use in comparison to the other response tools. The only negative outcome in the analysis was associated with water column exposure following dispersant use. This was significantly outweighed by the positive outcomes for the other resource categories that were evaluated.

FINDINGS AND RECOMMENDATIONS

Finding: Each response method has a complex suite of advantages and disadvantages, including and not limited to encounter rate, effectiveness, and ecosystem and human health effects, that are considered when selecting response options.

Finding: Experience with historical spills and integrated models consistently indicate that for large spills, dispersants (both subsea dispersant injection [SSDI] and surface) are a response option that can substantially reduce surface oil.

Recommendation: A metric should be developed which illustrates the impact of SSDI on moving the surfacing oil away from the well. In general, the greater the distance from the well, the better, except in cases where the oil surfaces in the vicinity of sensitive species or habitats.

Finding: Two detailed examinations of the use of SSDI in deepwater scenarios found that SSDI more effectively reduced surface oil than other options. However, it must be remembered that these results are site, model, and scenario specific.

Recommendation: A controlled field experiment or spills of opportunity should be used to collect comprehensive field observations for validating the entire integrated model.

Finding: The Spill Impact Mitigation Assessment (SIMA) and Comparative Risk Assessment (CRA) tools represent two new advances toward qualifying and quantifying the trade-offs involved with response options. The use of integrated models in the new SIMA and CRA tools provides a mechanism for assessing "combinations of response options deployed simultaneously," with particular focus on large-volume events, which is a considerable improvement over the Consensus Ecological Risk Assessment method, which is limited to a single response option at a time.

Recommendation: Ensure that the decision-making tools consistently and adequately address uncertainty in estimates of potential human health issues as well as environmental impacts. Investigate the sensitivity of various integrated models to biodegradation sub-models.

Recommendation: The benefits and impacts calculated by the CRA should be better validated by hindcasting past spills.

Finding: Integrated model case studies demonstrate that droplet size distribution (DSD) is a critical variable for properly estimating the fate and effects of oil and dispersed oil, especially in the event of a subsea release.

Recommendation: In order to improve models, consider the use of real-time measurements of DSDs at the source during a subsea event.

Recommendation: Develop a site-specific nomograph in site contingency plans that shows how DSD affects fates. This could facilitate an informed discussion on the merits and optimization of SSDI use.

Finding: All models to calculate oil droplet size in a subsea release have used at least one calibration coefficient that must be determined by comparing the model to observations. Only one of these models has been calibrated with more than 12 observations and validated with observations that were not used in the model calibration. There are now more than 200 high-quality experimental observations that can be used for model calibration and validation.

Recommendation: Models should be calibrated with many observations covering as wide a range as possible of oil properties, dispersant-to-oil ratio, gas-to-oil ratio, flow rates, etc. Once the model has been calibrated it should be validated using a different set of observations in order to estimate model bias and confidence limits.

CHAPTER 7

RESEARCH AND DECISION-MAKING PROTOCOLS

The purpose of this chapter is to review concepts considered in the other chapters and highlight protocols for studying, researching, or otherwise understanding these concepts. For each topic, this chapter outlines the state of the art, potential pitfalls, and emerging issues and advances. The objective of this synopsis is to aid regulators, stakeholders, and practitioners by serving as a synthesis of protocols, with the other chapters providing more detailed and technical background.

OIL FATE AND TRANSPORT

Environmental Geochemistry Research Protocols

State of the Art and Potential Pitfalls

The response efforts associated with the *Deepwater Horizon* (DWH) oil spill included the use of numerous techniques in environmental geochemistry with potential to inform response options, including dispersant application. A selection of geochemical applications and methodologies potentially useful in informing response options with quantitative results are the focus of this section. Key to the application of geochemical approaches is knowledge of the chemical composition of the spilled oil, which in the case of the DWH oil spill was not readily available. Thus, for major oil spill events in the future, spill response operations would benefit if all available information regarding the chemical composition of the spilled oil and applied dispersant was made publicly available, and if oil samples were also made available to the response and scientific communities (see Chapter 5).

Hydrocarbon and Dispersant Fractionation

Based on the benchmark of a source oil composition, environmental geochemical studies inform both fate and transport of discharged petroleum fluids and applied dispersant. A key metric for understanding the partitioning of oil and dispersant is the fractional abundance of a given chemical species, typically calculated as a normalized ratio, in which the compound of interest in the environmental sample (A_e) is referenced to a benchmark compound in that same sample (B_e), and then a ratio calculated in reference to the abundance of those same compounds in the source oil (A_s and B_s). The result is a fractional abundance relative to both the reference compound and the source oil.

$$F = \frac{A_e / B_e}{A_s / B_s}$$

By choosing a benchmark compound that is conserved relative to the process of interest, the resulting fractional abundance provides a robust tool to investigate the disposition of oil by effectively removing effects like dispersion, advection through open boundaries, etc. This double normalization approach, referred to here as geochemical referencing, was applied during DWH toward understanding the mass balance of oil, and it was key to understanding those processes that fractionated the discharge, including both physical partitioning and biodegradation. Seven applications of this approach during DWH are outlined here, each of which applies to a specific and limited time window.

- First, geochemical referencing was used to determine the fate of natural gas compounds—ethane and propane—relying on methane as a conservative benchmark (Valentine, 2010). This approach revealed that these gases were consumed in the deep intrusion layers and were the major contributor to deep-sea oxygen sags observed in theatre.
- Second, geochemical referencing enabled calculation of dissolution in the deep intrusion layers. This was accomplished notably for benzene, toluene, ethylbenzene, and xylene (BTEX) compounds (Camilli et al., 2010) by comparing aqueous solubility to fractional abundance for a range of compounds.
- Third, geochemical referencing was used to differentiate net aqueous dissolution of specific hydrocarbons relative to evaporation by reference to aqueous-insoluble compounds of comparable volatility (Ryerson et al., 2011). This was accomplished through atmospheric measurement.
- Fourth, geochemical referencing was used to identify the partitioning of the dispersant component, dioctyl sodium sulfosuccinate (DOSS) by reference to methane and to the environmental oxygen deficit (Kujawinski et al., 2011). These findings demonstrated that DOSS dissolved to the intrusion layers along with other soluble compounds.
- Fifth, geochemical referencing enabled a mass balance for DWH that included dissolution, evaporation, and subsurface trapping of oil droplets (Ryerson et al., 2012). This approach considered all available measurements as well as flow rate estimates but was enabled by geochemical referencing.
- Sixth, geochemical referencing was used to calculate the distribution of oil deposited to the seafloor (Valentine et al., 2014) as well as the rates, molecular patterns, and controls on biodegradation of oil deposited to the seafloor (Bagby et al., 2017).
- Seventh, geochemical referencing was used to estimate the trapping of liquid oil droplets in the deep intrusion layers (Gros et al., 2017) for a particular time period in June 2010. These results found that ~0.8% of the insoluble hydrocarbon fraction was trapped in the deep intrusion layers as microdroplets. Furthermore, by using geochemical referencing coupled with some reasonable assumptions about biodegradation, Gros et al. (2017) were able to estimate a mass balance through the overall water column that could be used to validate fate and transport models.

The methodologies needed for geochemical tracing of discharge as described here include a combination of traditional and evolving analytical tools, including Fourier transform ion cyclotron resonance mass spectrometry; liquid chromatography coupled to high-resolution mass spectrometry; comprehensive two-dimensional gas chromatography; compound specific isotope ratio mass spectrometry; and proton transfer reaction mass spectrometry. For a complex release scenario, the combined application of available methodologies warrants consideration by response personnel within the context of response operations, and expert scientific opinion can be essential in determining what value emerging technologies might provide. The timing of such measurements is also critical. Drawing from the DWH examples above, there is no single environmental sample that was analyzed comprehensively: for example, for the combination of surfactants; volatile organic compounds; BTEX; polycyclic aromatic hydrocarbons (PAHs); paraffins, isoparaffins, aromatics, naphthenes, and olefins; natural gases; biomarkers; and saturated alkanes. This is important because comprehensive analysis of samples would provide a comprehensive geochemical inventory that would robustly inform fate and transport processes.

Indirect Chemical Measurements

In addition to measurements of the spilled oil, including transformation rates and products, a number of indirect chemical measurements also proved useful during DWH. Specific examples include dissolved nitrogen species nitrate, nitrite, and ammonium (Chakraborty et al., 2012; Hazen et al., 2016; Lu et al., 2012); dissolved oxygen (Du and Kessler, 2012; Kessler et al., 2011a); dissolved phosphate (Hazen et al., 2016); and dissolved metals, notably iron (Shiller et al., 2017). Because each of these compounds is bioactive and follows predictable oceanic behavior, appropriate measurement schemes provided useful insight as to microbial growth and metabolism associated with hydrocarbons, including estimates for total hydrocarbon respiration in the deep intrusion layers (Kessler et al., 2011a).

Emerging Issues and Advances

Isotope Tracking

In addition to the quantification of compound concentrations described above, numerous isotopic methods proved useful in tracking the transport and fate of discharged materials during DWH; these and a number of emerging isotopic methods may prove useful in future spill scenarios. Isotopic tracing in the context of oil spills falls into three general categories. First is the measurement of isotopic abundance in specific discharged compounds for forensic identification and quantification of biodegradation. One specific application during DWH was to quantify the extent of biodegradation for methane, ethane, and propane (Valentine, 2010); numerous other isotopic systems—including sulfur, carbon, and hydrogen—have previously been applied to petroleum source identification (Peters et al., 2005). Various emerging isotopic systems also hold promise for petroleum spills, including compound specific sulfur (Amrani et al., 2009, 2012) and radiocarbon (Kessler et al., 2008a) quantification as well as clumped isotope analysis (Douglas et al., 2017; Stolper et al., 2015). Second is the use of isotopes as a tracer into other chemical forms. Specific applications during DWH included the tracking of stable carbon isotopes and radiocarbon abundance into biota (Chanton et al., 2012) and sediment (Chanton et al., 2014). Third is the addition of isotopes to environmental samples as a tracer to determine process rates or to identify the flow of carbon into the ecosystem. Specific application during DWH was to quantify oxidation rates of methane using tritium (Crespo-Medina et al., 2014; Valentine, 2010) and to identify microbes consuming select hydrocarbons with carbon-13 (Redmond and Valentine, 2012).

Intercalibration Experiments

An intercalibration experiment was performed to examine the measurement of oil hydrocarbons between 20 laboratories (Murray et al., 2016; Reddy et al., 2015). Results included measurements by gas chromatography, ultra high-resolution mass spectrometry, toxicity, shear velocity, and interfacial tension as well as the measurement of weathered oils using Fourier Transform ion cyclotron resonance mass spectrometry by a subset of labs. The reports recommended the use of certified reference materials alongside sample analyses and encouraged detailed reporting of methods and the associated quality assurance/quality control. While an intercalibration experiment has been performed only on oil hydrocarbons, the concept of this approach could be broadly applied for the measurement of all oil, gas, and dispersant compounds of interest.

Adoption of Emerging Technologies

An important lesson to emerge from the DWH oil spill is that developing technologies can provide critical insight into a complex spill scenario. Select examples provided above include in situ mass spectrometry linked to autonomous vehicle technology (Camilli et al., 2010); in situ mass spectrometry linked to an aerial platform (Ryerson et al., 2011); and development of new laboratory procedures by liquid chromatography-mass spectrometry for quantification of surfactants at trace levels. The application of these approaches has provided critical insight as to transport, fate, and impacts of oil and dispersed oil from this spill; yet, after 9 years, few of these analytical approaches have been formally adopted by the response community.

Biodegradation Protocols

State of the Art and Potential Pitfalls

The past decade has seen an increase in the use of molecular tools as direct (culture-independent) techniques to determine microbial community structure, functional capabilities of the environment, stress responses, protein identity and abundance, and the relationship between specific organisms and substrate compounds. This has been largely due to the rapidly declining costs of these methods from many thousands of dollars to only a few dollars per sample. In addition, the speed at which analyses can be performed has decreased from months to hours. Consequently, the number of known oil-degrading microbial phyla has increased dramatically (three phyla to seven phyla in all kingdoms) as our ability to detect them has increased. Currently, oil degraders are found in all three domains of life (Hazen et al., 2016). However, all these culture-independent techniques carry underlying assumptions and rely on analytical pipelines that build on biases for the final conclusion, so they must be scrutinized carefully for positive and negative controls, field trip blanks, and materials and methods (see Figure 7.1).

The DWH oil spill saw many new protocols used for the first time both in the field and in the lab. Many molecular techniques had not been tried extensively in the field, which raises concerns based on sample collection. Such concerns include:

- whether or not sample collection actually captured the desired subsurface feature, such as an intrusion layer;
- whether the samples were filtered at depth in situ or were collected in sampling bottles and brought to the surface for further processing (how were they handled, how long did it take to process them on deck, how were they stored);
- handling of the sampling bottle prior to processing can substantially change the microbial environment (e.g., temperature, pressure, and surface substrate of the bottle interior). For

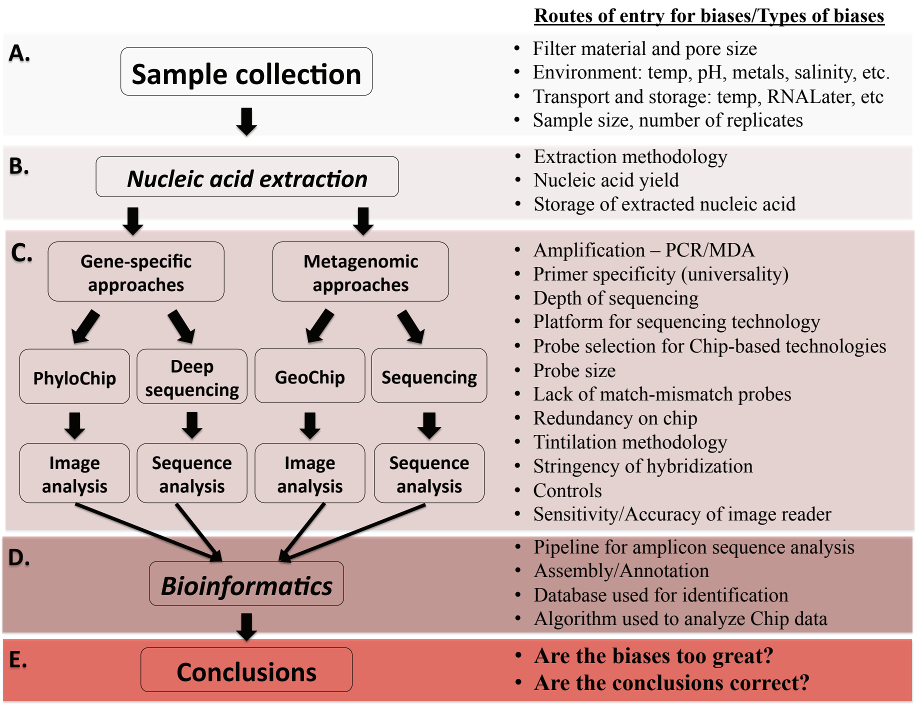


FIGURE 7.1 Pipeline of individual processes associated with culture-independent, nucleic acid-dependent approaches. Within steps A-E, biases are introduced and carried through, resulting in compounding bias. Biases introduced at earlier stages are further amplified by the end of the pipeline. Light color represents little bias and darker color represents increased bias. (A) Sample collection is the initial step in culture-independent approaches; (B) Extraction of nucleic acids; (C) Molecular techniques and analyses associated with culture-independent approaches; (D) Bioinfomatics; and (E) Conclusions. SOURCE: Hazen et al., 2013.

example, if samples were collected at 4°C and at high pressures, but were stored live on deck for more than just a few hours before being processed, the microbial community is likely to be different from that at the sampling site (Liu et al., 2017a); and

- collection of samples that could indirectly indicate biodegradation, such as sensitive dissolved oxygen measurements, direct cell counts, hydrocarbon fractionation (see the Hydrocarbon and Dispersant Fractionation section in this chapter), and isotope tracking.

Numerous studies published since DWH focused on oil biodegradation. Unfortunately many studies were done with samples collected and stored for weeks to years after they were collected (Bælum et al., 2012; Crespo-Medina et al., 2015; Dubinsky et al., 2013; Hu et al., 2017; Liu et al., 2017a). In addition, "open water" environmental conditions are impossible to fully replicate in the lab, and many studies were not conducted using Macondo oil and/or Corexit® 9500. Few studies used live oil (Jaggi et al., 2017). Most instead used dead oil or even non-crude oil. While some of these studies may have sound conclusions, it is possible that fresh live oil and samples from the Gulf of Mexico would have given different results. Furthermore, as noted by Yergeau et al. (2015), the timing of studies during and after the spill is also an important consideration for evaluating the potential for long-term effects. The concentrations of oil and/or dispersant used in these studies differed from the actual concentrations encountered in the field. For example, a study published by

Kleindienst et al. (2015b) suggested that "Chemical dispersants can suppress the activity of natural oil-degrading microorganisms." Yet, a later publication (Techtmann et al., 2017) suggested that "Corexit® 9500 Enhances Oil Biodegradation and Changes Active Bacterial Community Structure of Oil-Enriched Microcosms." Several factors differed between these studies including oil that was used, the microcosm setups, and the applied concentrations of oil and Corexit® 9500. Such divergent approaches create confusion when scientists, stakeholders, regulators, practitioners, and the public try to meaningfully interpret the results.

It is also unclear whether the biodegradation pathway sequence of oil is different in anaerobic seawater environments. Anaerobic biodegradation of hydrocarbons is a significant process that occurs in many environments (Gieg and Toth, 2018; Gründger et al., 2015; Laso-Pérez et al., 2016; Wawrik et al., 2012) and may be an important process in some deepwater communities of the ocean; however, anaerobic hydrocarbon degraders are primarily found in anoxic sediments and within ocean hydrocarbon seeps (Hazen et al., 2016; von Netzer et al., 2013). Anaerobic hydrocarbon degradation has been studied in fossil hydrocarbon reserves (e.g., tar sands; Berdugo-Clavijo and Gieg, 2014) and in thermophilic communities (e.g., around hydrothermal vents; Laso-Perez et al., 2016), but less knowledge exists about this process among cold-adapted communities in deepwater environments. In deep coastal environments where the temperature is nearly always 4°C, psychrophilic and psychro-tolerant microbes can play a significant role in oil biodegradation, even degrading oil faster than microbes in the surface water, as was seen in DWH (Hazen et al., 2010; Valentine et al., 2012). Thus, maintaining a proper temperature for microcosms and collecting samples and maintaining that temperature during transport and storage also become critical.

The potential for hydrostatic pressure to inhibit oil biodegradation is relevant to deepwater blowouts and to oils that sink to the deep-sea floor but has been largely overlooked. The Macondo well is located at a water depth of 1,500 m, which is shallower than the depth of 2,000 m beyond which pressure effects on biodegradation rates are expected (Hazen et al., 2016; Marietou et al., 2018). A recent study that considered oil biodegradation rates using samples collected during the response phase of DWH at pressures equal to 1,500 m found no effect, consistent with expectation; however, studies at higher pressure on the same samples did indicate that pressure might affect oil biodegradation rates and pathways (Marietou et al., 2018). In addition, many other factors may work synergistically to impact the biodegradation of oil (see Table 7.1).

The publicity of DWH led to inevitable comparisons to the *Exxon Valdez* oil spill. However, these spills were completely different in terms of oil type, the environment, and the use of dispersants. Other than the fact that both environments contained oil degraders, the two spills were not comparable in terms of biodegradation rates of oil (Atlas and Hazen, 2011).

In spill responses, scientists have observed the microbial biomass in the water column slowly decline long after the oil has been depleted. In DWH, many thought that this was due to the oil degraders surviving for an extended period of time (Dubinsky et al., 2013). However, detailed studies during and after the DWH spill demonstrated that the microbial community structure changed from oil degraders once the oil was no longer present to microbes that could use dead bacteria as a food source (Dubinsky et al., 2013).

Whole oil has an apparent half-life; half-life does not imply first order kinetics. Classification of different compounds in the oil and how they are degraded has been reported; some degrade very slowly, resulting in heavy oil (Aeppli et al., 2014; Head et al., 2014). The pathway for oil biodegradation was shown not to be altered by Corexit® 9500 both in the water column (Prince and Butler, 2014) and in sediment cores from DWH (radio-labeled constituents from Corexit® 9500 and whole oil, 5°C) (Mason et al., 2014). Nutrients and trace metal concentrations can regulate rates and pathways of oil biodegradation, especially in low nutrient environments like the oceans (Bælum et al., 2012; Hazen et al., 2016; Pepper et al., 2015). The microbial community composition will dictate which oil biodegradation pathways are used, how fast the oil is degraded,

TABLE 7.1 Synergistic Effects That Impact the Biodegradation of Oil

Factors Working Synergistically	Impact on Biodegradation
Chemical dispersants + mineral fines	Individually each will promote dispersion of the oil. Combined, the formation of daughter products and transfer of oil from the surface into the water column is enhanced.
Autoinoculation + “memory response” of hydrocarbon degraders	Introduction of hydrocarbons to previously exposed water parcels leads to an increase in microbial abundance and accelerated hydrocarbon biodegradation.
Oil droplet size + dispersion + biodegradation rates + dissolution	Enhances biodegradation, dissolution and dispersion rates of oil hydrocarbons.
Cometabolic biodegradation + dispersion + secondary electron donors	Enhances biodegradation, dissolution and dispersion rates of oil hydrocarbons even when the oil itself cannot be a suitable electron donor.
Biosurfactants from multiple microorganisms	Enhances bioavailability of poorly soluble compounds.

SOURCE: Hazen et al., 2016.

which compounds in the oil are degraded, and what oil daughter products might result, which could affect the bioavailability and toxicity of hydrocarbon compounds.

Emerging Issues and Advances

The emerging realization that oil biodegradation is a function of the environmental system as a whole represents a departure from compartmentalized research that provides an inadequate picture of oil biodegradation during a spill. Thus, an ecosystem services approach is required. The DWH oil spill was a prime example of one of the most rigorous oil spill sampling efforts ever undertaken, but the efforts failed to initially coordinate collection of all the components. It also failed to have a plan vetted by systems experts that would allow immediate deployment, including resources (money, equipment, and people) on standby for a large-scale spill response. These scenarios require that government agencies—for example, the National Oceanic and Atmospheric Administration (NOAA), the U.S. Coast Guard (USCG), the U.S. Environmental Protection Agency (EPA), and applicable state agencies—work together to develop a plan and designate contingencies for resources that could be used in that plan. The government oil spill response documents have been reviewed, with exercises carried out for people to work with. The governing documents for oil spill response include:

- National Response Framework[1]
- National Oil and Hazardous Substances Contingency Plan[2]
- Title 40 CFR 300.115—Regional Response Teams

None of these includes a complete systems approach; for instance, oil biodegradation should be part of any such field sampling plan that would also provide for follow-on laboratory studies that will be critical for the analysis and understanding of the fate and effects of the spilled oil. Figure 7.2 provides an overview of key aspects of that plan in a stepwise fashion to ensure the best

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[1] See https://www.fema.gov/media-library/assets/documents/117791.

[2] See https://www.epa.gov/emergency-response/national-oil-and-hazardous-substances-pollution-contingency-plan-ncp-overview.

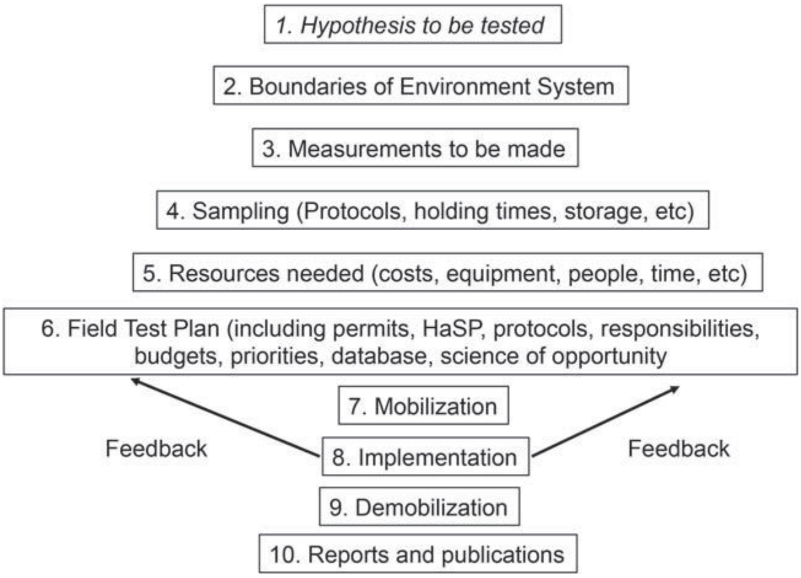

FIGURE 7.2 Environmental systems microbiology framework. SOURCE: Modeled after Hazen and Sayler, 2016.

possible outcome, recognizing that priorities will have to be set. The plan would be a dynamic living document with regular feedback from both the field and the laboratory.

As part of this Field Test Plan, development of a Data Management Plan could assure that all the data collected are in a format and location where they can be stored and used. The Gulf of Mexico Research Initiative (GoMRI) has developed the Gulf of Mexico Research Initiative Information & Data Cooperative (GRIIDC)[3] to capture all the data funded by GoMRI related to the DWH spill. The cooperative might be a useful starting point for this type of database. NOAA also has a database for spill-related data called Data Integration Visualization Exploration and Reporting (DIVER).[4] The U.S. Department of Energy also has been working on a database for all its funded projects for more than a decade and has made it public (KBase: The U.S. Department of Energy Systems Biology Knowledgebase).[5] KBase is “a collaborative, open environment for systems biology of plants, microbes and their communities,” which encourages investigations and findings from all environments. Integration across platforms is clearly something that should be recommended across government agencies, especially for GRIIDC, DIVER, and KBase. Figure 7.3 provides an example of culture-independent (not isolated and cultured) data types, measurements, formats, and priorities for environmental systems biology.

Improved understanding of natural biodegradation rates of oil and the effectiveness of chemical dispersants in the Arctic marine environment will be important as maritime transportation and oil exploration expand in the region (NRC, 2014).

A number of microcosm studies have recently been focused on quantifying changes in microbial structure and function and potential oil biodegradation rates in seawater and ice core

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[3] See https://data.gulfresearchinitiative.org.

[4] See https://www.diver.orr.noaa.gov.

[5] See http://kbase.us.

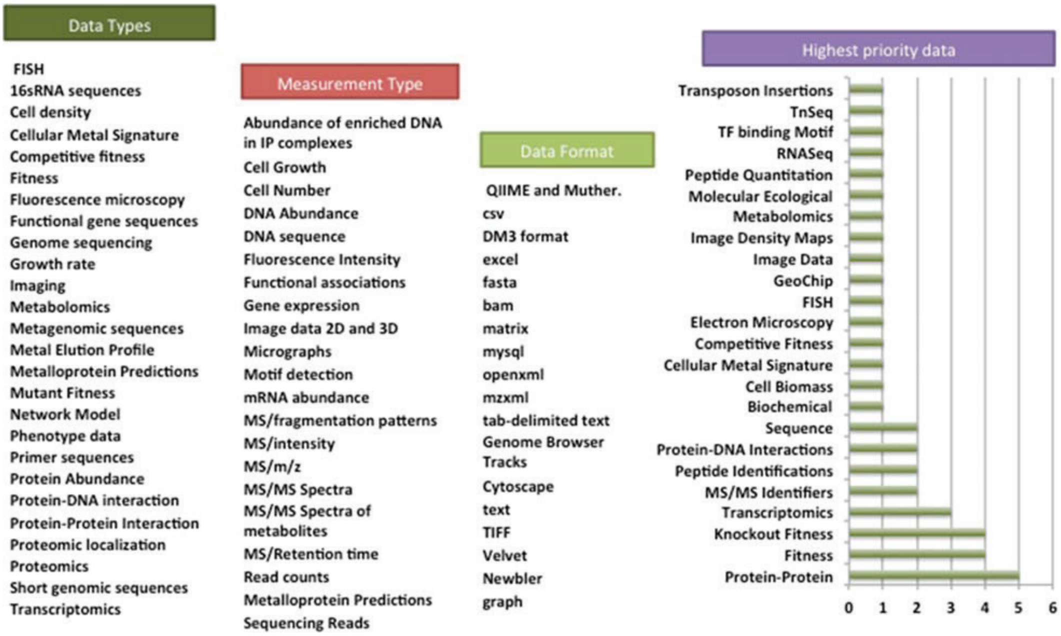

FIGURE 7.3 Example of data considerations and priorities for culture-independent analyses. Priorities are based on data needs for a system biology approach but also taking into consideration time and cost of analyses. SOURCE: Hazen and Sayler, 2016.

samples recovered from across the Canadian Arctic (Garneau et al., 2016; Yergeau et al., 2017). In terms of dispersants, McFarlin et al. (2014, 2018) have chemically quantified biodegradation and abiotic losses of Alaska North Slope crude oil and Corexit$^{®}$ 9500 in Arctic seawater samples and identified the microorganisms potentially involved in biodegradation based on shifts in bacterial community structure and abundance of biodegradation genes.

A recent study supported by NOAA and EPA on State of the Science of Dispersants and Dispersed Oil in U.S. Arctic Waters (CRRC, 2017)—with a large group of experts and public review—concluded that many of the uncertainties about biodegradation of oil can be attributed to reliance on laboratory studies that may not accurately reflect environmental conditions. The influence of major environmental parameters on these processes, including low temperature, nutrient concentrations, sea ice, sunlight regime, suspended sediment plumes, and phytoplankton blooms that characterize the Arctic, merits future investigation (Vergeynst et al., 2018a,b).

Modeling Biodegradation

State of the Art and Pitfalls

The modeling of the biodegradation of oil droplets in the water column builds on modeling work on the biodegradation of dissolved hydrocarbons in aquifers and liquid oil in sediments. In general, the rate of biodegradation of dissolved hydrocarbon components depends on their concentration in water, whereas the biodegradation of non-aqueous-phase liquid (NAPL) is assumed to depend on NAPL-water surface area and the physical properties of oil, namely, viscosity. There are numerous papers on the biodegradation of NAPL within sediments, and these laid out the foundations for the biodegradation of NAPL suspended in water.

NAPL Oil in Sediments

In this section, one finds the model developed by Nicol et al. (1994) as well as the first-order models of oil biodegradation presented by Venosa et al. (1996, 2010). Geng et al. (2014, 2015) presented a model for hydrocarbon biodegradation that accounted for nutrient concentration on the biodegradation rate using a Monod-type formulation. Various parameters were estimated, and they were found to be consistent with those obtained from wastewater treatment fields and dissolved hydrocarbons.

NAPL Oil in the Water Column

Venosa and Holder (2007) reported biodegradation studies of Alaska North Slope oil in laboratory flasks. They fitted first-order models to the oil mass in the flasks. Their results showed that chemically dispersed oil biodegraded faster initially, but the final extent of biodegradation was the same as that of physically dispersed oil. Yassine et al. (2013) modeled the biodegradation of dispersed oil using Monod kinetics and a quasi-steady-state approximation for the dissolution of low solubility hydrocarbons in the water column, where the oil dissolves before being biodegraded. Campo et al. (2013) conducted laboratory biodegradation experiments using south Louisiana crude and two microbial communities from the Gulf of Mexico, one obtained from the surface (meso) and one from near the Macondo well (cryo). They found that chemically dispersed oil biodegraded faster, and that the meso experiments resulted in faster biodegradation overall. The cryo experiments exhibited a lag ranging from 2 days to 28 days, and alkanes larger than n-C_{14} persisted in them while the aromatics of similar sizes were biodegraded. Campo et al. (2013) attributed the recalcitrance of the alkanes to the formation of crystalline structures of these alkanes. They fitted first-order models without lags to the biodegradation rates. The experiments were conducted at atmospheric pressure, which might not represent the optimal conditions for the cryo cultures. They also used extremely high concentrations of nitrate (2.8 g/L KNO_3) and phosphate (0.55 g/L NaP_3O_{10}), which were much higher than the concentrations at depth in the Gulf of Mexico (Hazen et al., 2010). Brakstad et al. (2015) conducted laboratory biodegradation experiments on two droplet sizes, 10 µm and 30 µm. They observed that the smaller droplets biodegraded faster. They also observed a lag that was generally less than 8 days, using coastal Norwegian seawater. Wang et al. (2016b) conducted a similar study, using GOMEX oil, but found situations where the 30 µm droplets biodegraded faster than the 10 µm droplets did. They also found a lag up to 10 days, but importantly, the samples were pretreated with oil for several weeks prior to experimentation, calling into question the relevance of the reported lag time. Using local Norwegian fjord seawater and local oil in the presence of methane, ethane, and propane, Brakstad et al. (2017) found that methane oxidation was faster than propane, which is the opposite that was found with DWH where propane jump-started the biodegradation process of the Macondo oil (Valentine et al., 2010). This suggests that biodegradation of oil and gas could be inherently different in varying environments.

Emerging Issues and Advances

The models used in the studies discussed in the previous paragraph did not account directly for the fact that biodegradation of dispersed oil occurs at the oil-water interface and thus increases with the oil-water surface area (Atlas and Hazen, 2011). In NOAA's Automated Data Inquiry for Oil

Spills model, the oil is assumed to consist of various pseudo-components (C_4-C_{12} alkanes, 2-3 ring aromatics, and others), and the biodegradation rate is assumed to depend on the surface area of the oil droplet. The size of the oil droplet is allowed to be reduced following biodegradation (Viveros et al., 2015). In a simulation developed by Vilcáez et al. (2013), the authors assumed oil droplets were completely covered by microorganisms. The results indicated faster biodegradation of small oil droplets due to their larger surface area per unit mass. Because the model assumes complete microbial coverage, the oil droplets biodegraded faster than the dissolved oil components, but no evidence was provided to support the assumption of total microbial coverage.

The impact of nutrients on oil biodegradation has been noted since the 1970s, and more recent studies found that concentrations exceeding a few mg-N/L of water are needed for maximal biodegradation rates (Boufadel et al., 1999). More detailed studies have elucidated that nutrient concentration was a limiting factor for the DWH oil biodegradation in surface waters (Atlas and Hazen, 2011; Bælum et al., 2012; Chakraborty et al., 2012; Dubinsky et al., 2013; Edwards et al., 2011; Hazen et al., 2010, 2016; Kimes et al., 2013, 2014; King et al., 2015a; Lu et al., 2012). The impact of nutrients has been modeled using a Monod type expression (Geng et al., 2014) for oil within sediments, and the model could be easily translated to dispersed oil. However, there are no calibrated models of dispersed oil biodegradation that incorporate the impact of nutrient and account for what has been observed. At low nutrient concentration, the rate of biodegradation of oil is proportional to concentration, and at high nutrient concentration, the rate reaches its maximum value and thus becomes independent of the actual value of the nutrient concentration.

Meso-Scale Test Facilities for Dispersant Studies

State of the Art and Potential Pitfalls

There are four major types of meso-scale facilities developed for the study of oil fate and behavior in the presence and absence of dispersants: (1) tower tanks for studying plume and oil droplet behavior from subsurface oil releases as well as oil component partitioning and gas droplet behavior; (2) flume tanks for studying weathering of oil and dispersed oil under various environmental conditions (e.g., currents, wind, temperature, and ice presence); (3) wave tanks with the capacity to provide controlled energy dissipation rates for oil droplet formation, oil fate, and transport studies; and (4) high-pressure test chambers to study the above variables under different pressure and temperature conditions.

These test systems do not fully replicate "open water conditions." Despite their relative size, enclosed systems such as these have a number of potential limitations, such as higher levels of oil droplet coalescence; the loss of oil from the water column due to changes in hydrodynamics; and biological responses related to containment and "wall effects" that preclude the determination of an accurate mass balance for the oil used in experiments. Furthermore, in terms of oil biodegradation studies, test facilities systems using artificial and recycled seawater do not have the normal microbiome of the ocean environments being simulated.

Tower Tanks

Data on oil droplet size and plume behavior for the development and validation of models have been collected from experimental studies using tower tanks. Since the DeepSpill field experiment in 2000 (Johansen et al., 2003), studies at the SINTEF Tower Basin (6 m high × 3 m wide, 40 m^3 seawater) in Norway and the CEDRE Experimental Column (5 m high × 1 m wide, 4.5 m^3 seawater) in France have have been largely responsible for data used in models to advance our knowledge on deepwater releases of oil. These test systems include an injection system that can control the release rates of oil and gas as well as instruments to monitor oil droplet and gas behavior (Brandvik et al., 2013, 2014b, 2017b, 2018, 2019a,b; LeFloch et al., 2013). Water samples are recovered at various depths for the analysis of total hydrocarbons, dispersant concentrations, content of oil-in-water (droplets and dissolved components), and interfacial tension analysis.

Scaling of oil droplet size data remains a challenge for the potential use of tower tanks due to limitations in the volume of oil that can be released and the diameter of the nozzle in the injection systems. Natural water column density gradients are not accounted for in these existing laboratory systems.

Flume Tanks

Flume tanks comprise a looped system in which water is continuously circulated and waves are generated to replicate field conditions. Over the last two decades, following the construction of the SINTEF flume tank facility in Norway (elliptical system, 9 m circumference, 0.5 m wide, 0.4 m depth, 4 m long major axis, containing 1.75 m^3 of seawater), there has been a continuous development of flume tanks for oil weathering and dispersant effectiveness studies. Constructed to simulate environmental conditions, the SINTEF flume tank incorporated a wave generator, submerged pumps, and fans to control water flow and wind effects as well as UV lamps for solar irradiance to enable photooxidation studies (Castro et al., 2016; Fiocco and Lewis, 1999; Hokstad et al., 1998; NRC, 2005).

Subsequently the "Polludrome" flume system was developed by CEDRE with a significantly larger canal (L = 12 m, W = 0.6 m, H = 1.4 m) with a total volume of 10.5 m^3. Expanding on the capability of the SINTEF flume tank, this system was connected to a large storage tank to enable the pumping of water into and out of the flume to simulate tides. It also had a long straight section that extended beyond the elliptical flume, in line with the wave generator, in which a shoreline could be constructed (Guyomarch et al., 1999; NRC, 2005). More recently, the system incorporated a solar radiation simulator capable of simulating the global range of solar exposure conditions and a laser particle size analyzer (Malvern Mastersizer 2000) for the collection of data on oil droplet size distributions (DSDs) (Guyomarch et al., 2012; NRC, 2005). Based on the success of the flume tanks at SINTEF and CEDRE, similar test systems have been constructed in Canada (i.e., SL Ross Environmental Research Limited, Ottawa, Canada), China, and the United States (pending). This network of test systems will be intercalibrated to enhance the intercomparison of results.

In 2018, Environment and Climate Change Canada completed the construction of the Canadian Environmental Oil Spill Simulator, a meso-scale testbed for spills of oil and other hazardous products in fresh and marine waters and in temperate and Arctic conditions. Containing 7.5 m^3 of water, at a depth of 0.9 m, in a channel 0.6 m wide, this system is based on the existing flume tanks located at CEDRE and SINTEF. Advances include automated control systems to support long-term studies for weeks to months, with full control of all conditions (e.g., waves, currents, temperature, salinity, solar irradiance, wind, rain, stratification, formation of surface ice, etc.).

Wave Tanks

The Ohmsett wave tank operated by the U.S. Department of the Interior's Bureau of Safety and Environmental Enforcement (BSEE) is the largest outdoor saltwater wave/tow tank facility in North America (see Figures 7.4 and 7.5). Recent works funded by BSEE have been aimed at characterizing the wavetank hydrodynamics (Boufadel et al., 2017) and chemistry (Boufadel et al., 2017). The effectiveness of various dispersants on surface oil was also explored, including a recent work by Steffek et al. (2016).

FIGURE 7.4 Overview of the Ohmsett facility showing the main test basin and the surrounding facilities. SOURCE: Ohmsett.

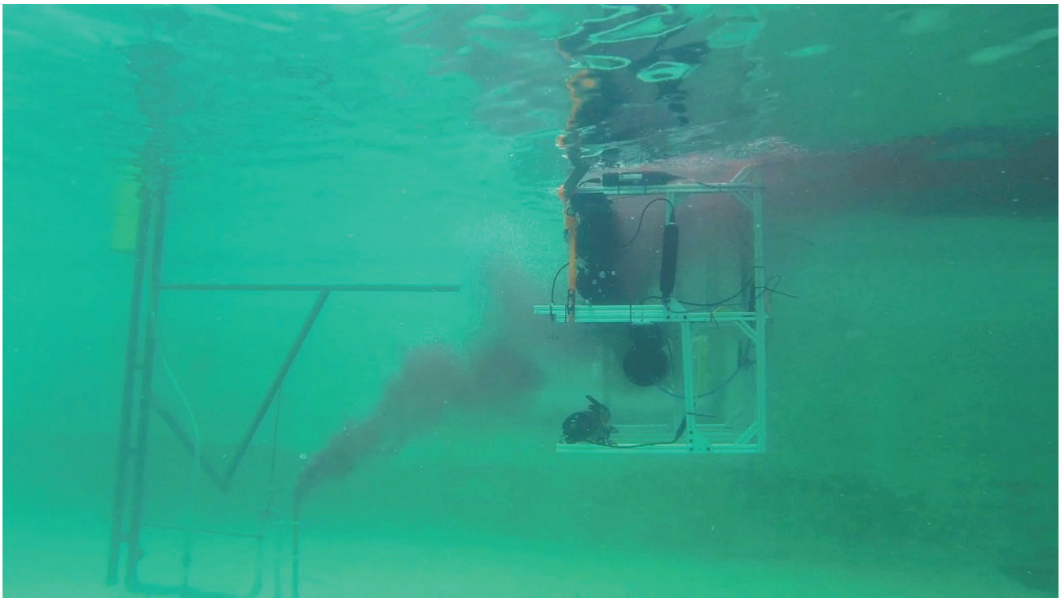

FIGURE 7.5 Experimental system setup for the towing of the vertical discharge pipe and instrument package as a unit to allow for plume dilution and the proper monitoring of oil droplets. SOURCE: Ohmsett.

Following the DWH spill, dispersant studies of subsurface releases of oil at Ohmsett have been performed in the presence of both oil and gas at dispersant-to-oil ratios ranging from 1:20 to 1:200 (Panetta et al., 2012, 2013). Biodegradation studies of oil and chemically dispersed oil are not conducted at the Ohmsett facility due to the need to chlorinate its water to control fouling by microorganisms.

The Ohmsett facility offers a versatile and flexible basin with its large horizontal dimensions (200 m × 20 m) but limited water depth (2.4 m). Attempts to overcome this limitation have been undertaken by Brandvik et al. (2017d) and Zhao et al. (2016d) by issuing the jet horizontally or by towing the jet horizontally to simulate a current. This raises the issue of fractionation, which deserves further consideration.

A joint effort funded by Fisheries and Oceans Canada and EPA, a wave tank facility was constructed at the Bedford Institute of Oceanography (Nova Scotia) in 2005 for the study of dispersants under controlled environmental conditions, including wave energy dissipation rates corresponding to conditions encountered at sea. The tank is also equipped with a series of manifolds to generate uniform water currents up to 0.5 cm/s along the direction of wave propagation to incorporate the effect of dilution and flushing on oil and applied chemicals that would occur in the natural environment (King et al., 2015c; Li et al., 2008b, 2009b). In addition, a suspended sediment load can be created in the tank to study oil and particle interactions (O'Laughlin et al., 2017a,b). Proximity to a ready supply of natural seawater and freshwater supply lines enable the simulation of coastal brackish water conditions within the wave tank facility. In operation 9 months of the year, experiments have been conducted in a range of water temperatures that are representative of seasonal variations in subarctic regions (~4°C to 20°C).

For studies on the fate and transport of subsurface discharges of oil, as well as surface spills in environments such as rivers where currents are stronger, a second tank of equal dimensions was recently built with a high flow pumping system capable of generating current velocities up to 5 cm/s and a pressurized oil injection system that can discharge heated oil at various flow rates through a nozzle in the bottom of the tank (Conmy et al., 2016, 2017; Li et al., 2016).

High Pressure Test Chambers

The influence of increasing water depth and hydrostatic pressure on droplet formation and dispersant effectiveness has been an intriguing question. The issue has been partially addressed by the use of a 5.6 m high, 2.3 m diameter hyperbaric chamber facility containing 24.4 m^3 of simulated salt water, located at the South West Research Institute in San Antonio, Texas (Brandvik et al., 2019b). Rated to a maximum pressure of 4,000 psi (275 bar) this system can be cooled down to 4°C, is fitted with instrumentation for the characterization of oil droplets, and it has a state-of-the-art delivery system for "live oil" injection. Analysis of oil droplet size from comparable experiments (nozzle, oil type, flow rates, injection techniques, and dispersant product) at ambient pressure (5 m depth) and high-pressure conditions (1,750 m depth/172 bars; such as are encountered by deepwater platforms in the Gulf of Mexico) showed no significant difference in droplet sizes as a function of water depth (Brandvik et al., 2019b).

A number of key experiments with oil and dispersants under DWH-simulated ambient conditions have also been conducted at the high-pressure facility at the Hamburg University of Technology (TUHH) in Germany. The nucleus of TUHH's High-Pressure Test Center is a 99 L stainless steel autoclave (see Figure 7.6), which provides the experiment space for specialized test modules. This pressure vessel has several hydraulic, electric, and mechanical interfaces that allow the manipulation of the experiments as well as the injection of fluids into the vessel. The pressure generation (maximum pressure of 55 MPa) is carried out by a pneumatic amplifier that compresses tap water and routes it into the main pressure vessel (Seeman et al., 2014). The experimental module for the

FIGURE 7.6 High-pressure test center at the Hamburg University of Technology. SOURCE: Hamburg University of Technology.

investigation of DSDs ("Jet Module") consists of an acrylic cylinder (190-mm inner diameter, 600 mm height) filled with artificial seawater that can be placed within the high-pressure steel autoclave. The autoclave is then filled and pressurized with tap water. Pressure equalization occurs through a flexible membrane connected to the acrylic cylinder, thereby creating isobaric conditions between test volume (within the acrylic cylinder) and autoclave. Oil or gas is released into the test volume via a 1.5 mm nozzle from a pressurized reservoir positioned outside the autoclave (Malone et al., 2018; Seeman et al., 2014). The Jet Module is equipped with several temperature and pressure sensors to monitor conditions both within the seawater and in the oil reservoir. Oil and gas flow is monitored by a Coriolis mass flow meter. Data are recorded at a sampling rate of 300 Hz; sampling rates up to 24 kHz are possible (Malone et al., 2018). Endoscopic cameras measure DSDs and behavior. An important advance with this facility is the ability to test "live" (e.g., methane-saturated) oil and to simulate realistic effects of pressure drops as occur during actual deepwater blowouts. Gas-saturated oil droplets fracture into many smaller droplets when such pressure drops are simulated, consistent with observations of a similar magnitude pressure drop at DWH (Malone et al., 2018).

The accuracy of modeling tools for the depiction of deep-sea oil spills and the prediction of the ensuing three-dimensional distribution of the hydrocarbons in the ocean relies on precise input parameters. One of the most important influencing quantities to be determined is the rise velocity of the fluid particles originating from the blowout. To meet this challenge, a high-pressure countercurrent flow cell has been designed, constructed, and commissioned at TUHH in collaboration with the company Eurotechnica GmbH, Bargteheide, Germany, to conduct experimental investigations of bubble and droplet rise behavior under simulated deep-sea conditions using substance mixtures of interest. Varying combinations of pressure (up to 15 MPa) and temperature (4°C to 35°C) have been investigated for different systems (i.e., pure and methane-saturated crude oil in artificial seawater) (Malone et al., 2018; Pesch et al., 2017).

Field Studies

State of the Art and Pitfalls

As noted throughout this report, it is challenging to simulate many of the important complexities of a real spill in the laboratory or in a mathematical model. For instance, hydrodynamic processes measured in the lab must be scaled to the field, and this requires various assumptions. As another example, it is extremely challenging to conduct lab studies of oil effects on large animals or those living at high pressure.

Given the limitations of laboratory and model studies, numerous attempts have been made to take measurements during actual spills (what we will refer to as "Spills of Opportunity," or SOOs), and there have been several dedicated field studies, such as DeepSpill (Johansen et al., 2003) and Tropical Oil Pollution Investigations in Coastal Systems (Renegar et al., 2017b). While field studies capture more of the real-world complexity than do lab or model studies, they have their own set of challenges, which include:

1. Legal and Regulatory. A dedicated oil spill field study must receive authorization to purposely release oil into the environment and this is often a daunting undertaking. In the case of a SOO, scientific activities are also inherently limited by safety concerns and the fact that experiments cannot interfere with the response efforts and there is a concern about liability for the relative portion of natural resource damages.
2. Logistical Constraints. Conducting an experiment in the open ocean presents many logistical challenges, especially in the case of a SOO where science will always have lower priority than safety and response activities. Access to the casualty site is a frequent constraint (e.g., in a blowout, droplet size should be measured near the wellhead), but the response operators are reluctant to allow such access for fear that it will interfere with the well control operations.
3. Uncontrolled Complexity. In the lab, a scientist can reasonably hope to control or monitor all the important variables that could affect the experiment's outcome. That is not the case in a field experiment and even less so in a SOO. In the latter case, a scientist may not even have baseline data, and by the time scientists are on scene, it may be too late to collect relevant information.
4. Size. Even a modest-sized spill can cover huge volumes of ocean with open boundaries often dominated by complex currents, winds, etc. Monitoring all the potentially important variables with sufficient temporal and spatial resolution is costly at best, and frequently impracticable. For instance, doing a simple mass balance of oil in the water column during a blowout is a significant logistical challenge even in a modestly sized dedicated field experiment.
5. Cost. The cost of a field study in the open ocean is high. This can limit the duration of the scientific program, the spatial and temporal resolution, and the ability to systematically study the sensitivity of the dependent variables of interest to changes in independent vari-

ables. For a SOO, replicated scientific sensitivity studies are unlikely, though sometimes conditions do fortuitously provide for them.

In the case of a SOO, another challenge is to initiate the monitoring in a timely manner. It will usually take days or weeks to get the necessary scientific equipment in place to get meaningful measurements of an unanticipated spill. Key information can be lost during this preparation period. Of course, the time delay can be substantially decreased by pre-positioning monitoring equipment such as outlined by Aurand et al. (2001, 2004), but to the committee's knowledge, no one has ever executed such a program on a large scale. A major reason for this is that substantial spills are fairly rare occurrences and few funders or investigators are able to maintain standby capacity for long periods of inactivity.

DWH is the most recent example of a SOO in which many scientific observations were taken. However, the limitations of this dataset are numerous and well documented in the preceding chapters of this report. Although the DWH dataset does shed considerable light on many important science questions, it has left a long list of key unanswered questions. This outcome illustrates the difficulty of overcoming many of the limitations outlined above.

Emerging Issues and Advances

Despite all the challenges of conducting a dedicated field experiment or monitoring a SOO, there are numerous reasons why these efforts are worthy of consideration. Some examples identified in this report are:

1. Validation of integrated models. As noted in Chapter 5, integrated oil spill models are widely used to calculate the fate of oil and more recently to calculate the effects on biota. The integrated models are composed of sub-models, many of which have been validated to some degree, but the models as a whole remain poorly validated because of a paucity of high-quality, unambiguous datasets from actual spills. This is especially true of the newest generation of integrated models which incorporate effects.
2. Validation of droplet size models. As discussed in Chapters 2 and 6, oil droplet size is possibly the single-most important factor affecting the fate of oil in a blowout. Much work has been done in improving droplet size models, but the question of how well these models scale up to the field remains largely unanswered. Field-scale measurements are probably impossible to make in the laboratory; yet, with recent advances in key instrumentation (e.g., Davis et al., 2017), such measurements are now feasible in the field.[6]
3. Health impacts on response workers. One cannot purposefully expose humans to most of the substances a response worker encounters during an actual spill. Thus, a SOO is a unique chance to take measurements of real-world concentrations of oil spill pollutants and their effects on workers. As pointed out in Chapter 4, many questions remain concerning the concentration and effects of various pollutants on workers.
4. Validation of response decision-making tools. A number of semiquantitative approaches (e.g., Consensus Ecological Risk Assessment, Spill Impact Mitigation Assessment, etc.) have been developed to assist responders in considering trade-off decisions when faced with choices of response options, especially considering the use of surface- or subsea

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[6] It should be noted that there are many other questions concerning droplet size that can probably be answered more economically in a large-scale lab facility. These questions concern the dependence of droplet size on blowout preventer pressure gradients, degassing of live oil, churn flow, and tip streaming. Indeed, these phenomena could be very difficult to study in the field because of logistical and cost constraints. Hence, the reason for the call for the development of a large-scale lab facility in the recommendations of Chapter 2.

dispersant injection (SSDI)-based dispersant applications. Field-scale experiments can assist in understanding whether such apparent trade-offs are true or false dichotomies by observing system behavior under differing response approaches.

5. Systems approach to determine hidden effects. Because an ecosystem is greater than the sum of its parts, simplified lab studies can miss hidden synergies and complexities that occur in the real world. Modern advances in sensors and molecular techniques now make it much more probable that a careful field study can uncover these complexities.

Validation of Droplet Models

State of the Art

Since the DWH spill, a great deal of work has been done on developing models of oil droplet sizes emanating from a deepwater blowout. Chapter 2 shows that for DWH-like scales there is a discrepancy of up to four times between the three models examined.

Emerging Issues and Advances

All the existing droplet models reviewed in Chapter 2 use one or more tunable coefficients that must be determined by comparing the model results to observations and backing out the tunable coefficients using some kind of error minimization. This is commonly called the calibration step. Sound statistical practices then dictate that the next step should be to use these coefficients and compare the model against a totally new set of observations, preferably covering a different range of diameters, flow rates, etc., than the observations used to calibrate the coefficients. This is commonly referred to as the "validation" step, and it can be used to estimate the confidence limits on the model droplet size estimates. A close review of the papers describing the models shows that they have often stopped at the calibration step and have generally based their calibration on a small subset of available observations. In Chapter 2, the committee provides a recommendation that existing and future models be more thoroughly calibrated and validated, using the wealth of experimental observations now available, and that validation should be continued as new observations become available.

Another issue affecting droplet model accuracy is the lack of droplet observations during realistic blowout conditions, especially with SSDI activated. Without such observations it is hard to validate a droplet model but, more importantly, to establish the accuracy of the various models at full field scale. As noted in a Chapter 2 recommendation, there is a need to do further large-scale droplet measurements.

ENVIRONMENTAL AND AQUATIC TOXICITY

Toxicity Testing

State of the Art and Potential Pitfalls

It is important to note that a more extensive discussion of toxicity testing protocols can also be found in Chapter 3. The primary difficulty with the current state of toxicity testing is the improper use of test designs that are appropriate for a single compound for which the dissolved concentration can be separated. Oil is a partially miscible mixture of many components of widely varying solubility and toxicity. The dissolved components need to be measured and aggregated into a proper dose metric.

Toxic units (as discussed in Chapter 3) have been demonstrated to properly weight each component and is a proper dose metric. However, the commonly used arithmetic sum of either total petroleum hydrocarbons (TPHs) or the sum restricted to only the polycyclic aromatic hydrocarbon (PAH) concentrations (Total PAH, or TPAH) is not a proper weighting because (1) TPAH ignores all the other hydrocarbons that are contributing to toxicity, and (2) TPHs and TPAH ignore the orders of magnitude difference in all the component toxicity because they weight them equally (Equations 2-4 in Chapter 3). Therefore, neither TPH nor TPAH, even if they used dissolved concentrations, is a proper dose metric.

The usual water-accommodated fraction (WAF) preparation methods leave a residual of undissolved microdroplets as well as the dissolved concentrations. These microdroplets greatly complicate the analysis of the toxicity test results for two key reasons. First, measuring the concentration in the WAF includes both dissolved and microdroplet components, which substantially overestimates the concentration of the less soluble components. Second, when the WAF is diluted, it is assumed that concentrations decrease in proportion to the dilution. While this is true for the total (dissolved + microdroplet) concentration, it is not true for the dissolved fractions, because concentrations are elevated by the dissolution of the components in the microdroplets. The elevation can exceed orders of magnitude in concentration (see Chapter 3, Figure 3.14a). Because this effect depends on the concentration of microdroplets in the WAF, it covaries with other test variables (e.g., presence versus absence of a dispersant). If the microdroplet effect is not properly quantified the results of toxicity test cannot be unambiguously assigned to the effect being investigated (e.g., whether the dispersant increases toxicity).

Protocols for the Preparation of WAFs

Prior to the DWH spill, Chemical 67 Response to Oil Spills Ecological Effects Research Forum (CROSERF) protocols (Singer et al., 2001) had been in place to describe the best practices for the preparation of WAFs and chemically enhanced WAFs (CEWAFs) for use in toxicity testing. As described by Singer et al. (2001), “test media must be reproducible over time and between laboratories with standardized analytical methods to characterize the oil and quantify its components.” When mixing the dilution water and oil, the duration and energy must be sufficient to ensure equilibration of the dissolved mixture constituents in the water. The intensity of the mixing energy also influences the composition of the WAF; therefore, WAF/CEWAF preparation protocols need to generate solutions that are reproducible, comparable to earlier data, and sufficiently relevant to field conditions to be usable in risk assessments and other oil spill decision-making tasks.

Since 2010, a variety of new methods were developed that resulted in a myriad of different media preparation protocols. Adams et al. (2017) reviewed the oil mixing system (the equipment and/or method used to prepare test solutions) in 144 published toxicity tests and found a total of 226 mixing methods to generate solutions. The most common mixing instrument or method was the magnetic stirrer, and CROSERF was the most common method stated. However, a variety of other mixing methods, including commercial blending, hand mixing, orbital shaking, propeller mixing, pump mixing, sonication, upwelling dilution, and water recirculation, were also identified, and there were studies where the mixing method was not specified. These are depicted in Figure 7.7.

In addition to the type of mixing methods that have been employed in recent years, there have been numerous modifications to the CROSERF method to create new types of WAFs. In a 2013 paper (Incardona et al., 2013), the authors state that the high-energy WAF (HEWAF) standardized protocol was intended to produce WAFs that more closely emulate the dispersion of oil droplets under high pressure (i.e., the DWH spill). Studies conducted in 2017 to further examine HEWAF were done by making serial dilutions from a stock solution; however, only the stock solution was analyzed via fluorescence in order to reduce analytical testing (Forth et al., 2017a).

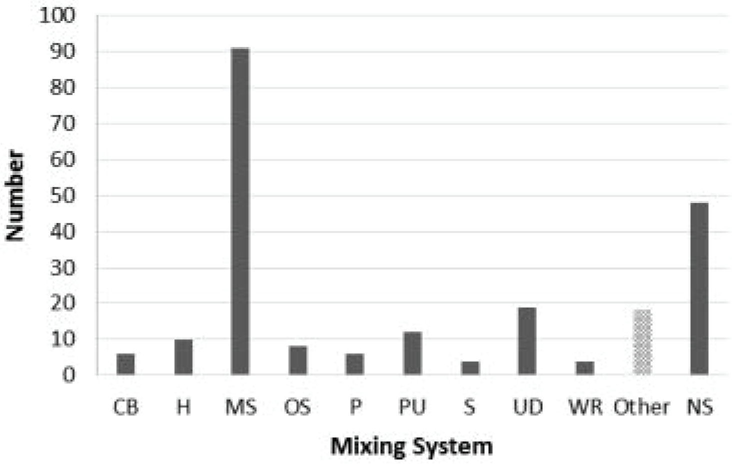

FIGURE 7.7 The number of toxicity tests that used a particular mixing system to prepare stock and test solutions of oil in water. Some studies used more than one mixing system in a single experiment (N = 226). NOTES: CB = commercial blender; H = hand mixing; MS = magnetic stirring; NS = mixing system not specified explicitly in the publication; OS = orbital shaker; Other = mixing systems occurring three or fewer times in publications; P = propeller; PU = pump; S = sonicator; UD = upwelling dilution; WR = water recirculation. One paper was omitted as there was no mixing of oil and water. SOURCE: Adams et al., 2017.

Another research team suggested that the HEWAF method required further standardization (Sandoval et al., 2017). This study examined three key factors: the presence or absence of oil microdroplets; dispersion stability over the time interval used in toxicity testing; and the chemical composition (PAHs) in relation to potential environmental relevance. This team determined that the CROSERF method for WAFs and CEWAFs had greater stability and were more representative of both dissolved components (WAFs) and oil-water mixtures containing microdroplets (CEWAFs).

Yet a third team (Stubblefield and De Jourdan, 2017) characterized test solutions of even more types of WAFs, including low-energy; no-energy; medium-energy; and intermediate-energy in addition to HEWAFs. Given the large differences in the various WAF composition, the authors concluded that it is imperative to accurately characterize and quantify exposures both in the laboratory and in the field to assess potential environmental impacts. The authors also concluded that adequate chemical analysis is required to generate data for empirically based toxicity models (e.g., the target lipid model and PETROTOX; see Chapter 3 for a detailed discussion).

Emerging Issues and Advances

A large quantity of experimental toxicity data is available that could be analyzed to continue to investigate the question as to whether exposure media containing chemically dispersed oil is more toxic than is media containing physically dispersed oil. Most of these data are from variable dilution preparation methods. The analysis would need to include a quantitative estimate of the microdroplet concentration at each dilution, estimates of the dissolved concentrations, and the use of toxic units as the dose metric. Methods are available to do this analysis. Chapter 3 provides a more detailed discussion of the problems that can occur when using different media preparation methods, and the reader is encouraged to review that information.

One promising new protocol for oil dosing, known as passive dosing, could potentially eliminate the confusion caused by use of varying WAF methods (see Chapter 3 for details). The added advantage of this approach is that it minimizes the interference introduced in toxicity data by oil microdroplets, thus generating exposures based on truly dissolved components that partition through permeable membranes. These soluble fractions are known to the primary drivers of hydrocarbon toxicity.

HUMAN HEALTH

Consideration of Human Health in Oil Spills

State of the Art

Integration of human and ecological health continues to be a major topic of interest among scientists and policy makers, including efforts by the National Research Council particularly aimed at coastal areas (IOM, 2014; NRC, 2013) and by federal agencies (Sandifer et al., 2015). These reviews focus primarily on understanding the role of human activities in degrading coastal and oceanic ecosystems as well as the value of a healthy ocean and coast in supporting human health and well-being.

However, oil spills and the response to oil spills present a slightly different challenge, but they nevertheless require a similar systems approach that integrates across multiple disciplines.

Existing Net Environmental Benefit Analysis tools like the Spill Impact Mitigation Assessment or the Comparative Risk Assessment (see Chapter 5) do not consistently include human health. Some have argued that it is unnecessary because human health considerations override all others throughout an oil spill response. There is extensive literature about the challenges of integrating human health considerations in standard Environmental Impact Statements (EISs). These include debates about whether human health is best incorporated within an EIS or should be separate in the form of a Health Impact Analysis or similar instrument. Deciding how best to incorporate health into the systems approach, which is the basis for effective decision making in response to oil spills, has begun and merits further consideration.

Potential Pitfalls and Methodological Challenges

Study of the potential impact of environmental factors on human health presents a number of methodological challenges (see Chapter 4) that are at least partially distinguishable from studies of ecosystem effects. These include:

- an inability to perform a fully controlled epidemiology study for environmental risks;
- implications of health effects in individual humans;
- implications of the wide variety in human vulnerability; and
- ethical issues particularly germane to human studies.

Epidemiology Studies for Environmental Risks

The gold standard for epidemiological methodology, the double-blind randomized controlled trial, is not possible for usual environmental epidemiology. A randomized controlled trial of a potential therapeutic agent for a specific disease usually consists of randomly assigning half of a group of volunteers with the disease to the agent and the other half to a placebo. The participants are not aware of which group they are in—nor is the medical team. Endpoints indicative of therapeutic efficacy and toxicity are then compared between the two groups. This controlled experimental design is not possible for environmental epidemiology for which most studies take advantage of uncontrolled differences in exposures. Whether the difference is geographical or temporal, numerous potential confounding factors limit interpretation of any observed association between cause and effect. Accordingly, the acceptability of a cause and effect relationship is often determined by having multiple studies that replicate the original finding, preferably performed by different investigators using different methodology in different populations with different sources of exposure to the agent of concern. Determining the potential human health impact of dispersant use during an oil spill, which is not predictable as to place and time, is very challenging. Also crucial to acceptability of an observed association is the biological plausibility of the association for which toxicological studies in laboratory animals or in vitro are central. The criteria involved in considering causality are usually assigned to Bradford Hill (Hill, 1965; Schünemann et al., 2011).

Implications of Health Effects in Individual Humans

Consideration of trade-offs is central to response decisions (see Chapter 5). In general, the health of individual humans carries greater weight than does the health of individual members of an ecosystem, although not necessarily to an entire ecosystem, which arguably itself has benefits to human well-being. The oil spill response process clearly guides the Response Coordinator to avoid obvious risk of adverse human health consequences, but the trade-off is less clear when it is between ecosystem effects and a lower level of human health risk to workers and to community members, particularly among those who suffer from preexisting conditions that increase their vulnerability.

Issues related to the wide variability in human vulnerability also include the difficulty in extrapolation of epidemiological and toxicological findings to those at highest risk. Vulnerable populations of particular societal concern include pregnant women and young children. Workers who enlist in the response effort may have preexisting health conditions that are not adequately determined prior to joining this workforce. While toxicological studies are valuable in comparing the relative toxicity among dispersants, extrapolating from animal or in vitro studies to humans, and particularly to vulnerable populations, presents challenges.

Ethical Issues Germane to Human Studies

Before beginning a study of workers and community members potentially affected by an oil spill, approval is required of an Institutional Review Board (IRB) that has the goal of protecting the welfare and privacy of all human subjects. Furthermore, the study must comply with the Health Insurance Portability and Accountability Act privacy rules. IRB approvals require significant planning. For an oil spill this is complicated by the fact that often the most effective approach requires collaboration among multiple academic and governmental institutions, each one having its own IRB that must approve the protocol in advance. After the difficulties encountered for the DWH studies, the National Institute of Environmental Health Sciences (NIEHS) and the Centers for Disease Control and Prevention have worked on developing off-the-shelf documents that can speedily be adapted for the next oil spill.[7]

Emerging Issues and Challenges to Exposure Assessments for Dispersants

Delays due to the need for IRB and other clearances specific to human studies are among the challenges to assessing human exposure resulting from an oil spill as compared to studies of

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[7] See https://disasterinfo.nlm.nih.gov/content/files/RAPIDD%20Protocol_v8.0_2015-07-16_508_CLEAN.pdf.

nonhuman biota. Biological markers of exposure which can be detected in human blood or urine can be particularly useful in determining the extent of exposure to crude oil components, including some for PAHs that have been recently developed in NIEHS-supported studies (Huang et al., 2014) and an analytical method for DOSS that conceivably could be useful in evaluation of human-derived biospecimens (El Said et al., 2010; Flurer et al., 2010). As a rule, however, biomarkers relevant to oil spill response only persist in the human body for short time periods. Accordingly, significant delay in initiating studies, as happened following the DWH spill, preclude dependence on biomarkers.

Delays in starting the studies also complicate the ability of workers to clearly remember whether they were exposed to dispersants when filling out a questionnaire at a later date. The accuracy of questionnaire responses is also complicated by a number of other factors. These include the fact that the response to potential exposure to dispersants does not substantially differ from that to crude oil and its derivatives, being dependent on similar good industrial hygiene practices. This means that in the relatively hurried nature of any spill response, keeping track of whether dispersant was potentially present may not be sufficiently important to inform the worker.

Questionnaire studies also are notoriously susceptible to what is known as recall or response bias. In situations of uncertainty, people are more likely to respond positively to questions about potential exposure, particularly when the issue has been publicized as one of concern—such as with dispersants. It is unclear as to whether the possibility of future litigation leading to funding for those exposed may contribute to recall bias in a situation such as the DWH spill response.

Development of badges or other monitors of dispersant exposure may be helpful for future exposure studies of workers or of community members.

Indirect Implications of Dispersant Use on Worker Health and Safety and on Community Health and Resilience: Temporal Factors

A major but indirect health impact of an oil spill is on the psychosocial health and resilience of communities suffering from concerns about their health; about the shorter-term economic, cultural, and environmental impacts; and about the possible long-term implications of the existence of an offshore oil industry. It is a reasonable assumption that the duration of both the oil spill and the resultant response activity is directly related to the extent of adverse psychosocial effects on individuals and communities. If, in fact, dispersant use speeds up the recovery process, presumably it would mitigate against longer-term psychosocial impacts and will improve community confidence in their longer-term prospects. Similarly, the risk of worker injury and illness presumably is related to the duration of response activities.

Implication of Dispersant Use on the Toxicity of Crude Oil Components: Benzene and PAHs

The carcinogenic components of crude oil are benzene and PAHs. Benzene is relatively volatile such that exposure of workers and, less likely, of community members would occur via inhalation. PAHs generally remain in the water. As PAHs are of concern because of their uptake into seafood eaten by humans, closures of fisheries—with attendant psychosocial, economic, and cultural impacts—are particularly problematic. Dispersants change the distribution of crude oil components, enhancing the dissolution of both PAHs and benzene. Greater dissolution of benzene in the water column could reduce the health risk to responders exposed to the volatile oil components in the air. Conversely, increased PAHs in the water column could raise the level of PAHs in seafood species, thereby affecting fishery closures and seafood consumption. As an additional complication, dissolution may differ depending on the avenue of delivery of the dispersant (e.g., subsea versus surface) or other local factors. While there is some inferential evidence that benzene is more likely to remain in water rather than be volatilized with subsea dispersant application, the committee was unable to find equivalent evidence of a change in PAH levels in seafood as a result of dispersant use.

TOOLS FOR OIL SPILL RESPONSE DECISION MAKING

Risk Assessment Tools

State of the Art

The Distinction Between Operational Versus Environmental Monitoring

Monitoring during an oil spill response is typically divided into two different categories:

- Operational Monitoring (or Type I monitoring), which collects near real-time data that are directly relevant to ongoing response operations or are needed to evaluate ongoing response strategies; and
- Environmental Monitoring (or Type II monitoring), which may include short- and long-term damage assessments, surveying recovery, and other purely scientific studies during and after an oil spill.

The Australian Maritime Safety Authority (AMSA) Spill Monitoring Handbook (AMSA, 2003) provided a comprehensive overview on all aspects of spill monitoring—both operational and environmental. AMSA released an updated Oil Spill Monitoring Handbook in 2016 (AMSA, 2016; see Figure 7.8). In 2013, both the API (2013) and the National Response Team (NRT, 2013) released guidelines focused on dispersant and dispersed oil monitoring. The API plan was specific to SSDI, while the NRT plan addressed both surface and SSDI.

In 2014, a multi-organization team in the United Kingdom released a guide for monitoring subsea oil releases and dispersant releases in UK waters (Law et al., 2014), and a review of new and emerging monitoring technologies suggests that future operational monitoring may be greatly assisted by use of unmanned, remotely operated, and autonomous surveillance equipment.

The underlying theme in these spill monitoring documents is that a good operational monitoring plan should incorporate the elements in shown Figure 7.8.

Shipboard Dispersant Operational Monitoring Protocols

During the DWH oil spill, a sizable number of assets (ships, equipment, and personnel) were deployed for operational monitoring, environmental effects monitoring, and damage assessment monitoring. While many of the latter studies (effects and damage assessment) were initiated later into the response (weeks or months after the spill response had started), operational monitoring was initiated within days of spill onset. Operational monitoring is intended to directly inform operational decision making during the response. There are several key elements to a dispersant operational monitoring plan. They include being:

- rapidly deployable;
- flexible and allowing for “phased deployment” based on needs and operational timelines;
- scientifically based;
- robust, using existing, proven technologies; and
- clear as to “action thresholds” for continued dispersant response operations.

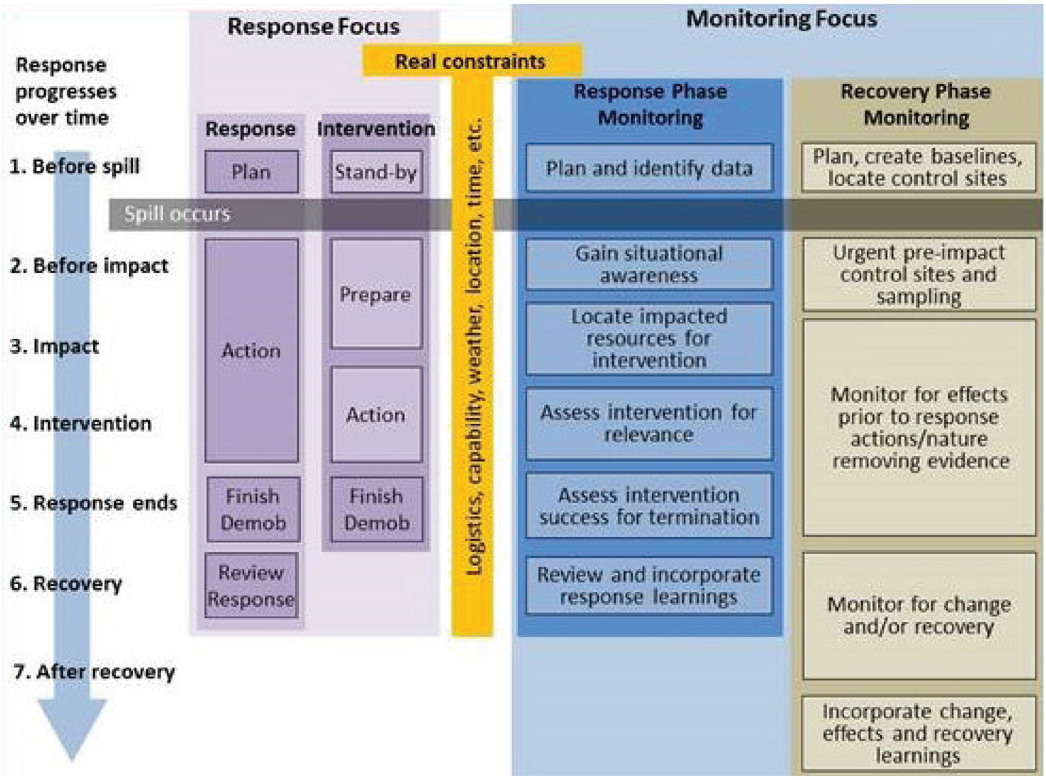

FIGURE 7.8 Description of monitoring by stage of the spill. SOURCE: AMSA, 2016.

Potential Pitfalls

In 2013, two sets of guidelines were published for dispersant operational monitoring. The API guidelines, *Industry Recommended Subsea Dispersant Monitoring Plan* (API, 2013), were specific to subsea dispersant injection. The NRT guidelines, *Environmental Monitoring for Atypical Dispersant Operations*, included guidance for both subsea dispersant injection and prolonged surface dispersant application (NRT, 2013). Both documents are intended to support development of operational, incident-specific monitoring plans, but they have often been confused with the USCG Special Monitoring of Applied Response Technologies protocols that are aimed at monitoring surface dispersant application at smaller, ephemeral oil spills. Having three different dispersant monitoring documents, authored by different organizations and with varying procedures for data collection and reporting, can be problematic.

While both the API plan and the NRT plan focus on operational monitoring, some data collected under the NRT plan could be made available for damage assessment purposes. Merging operational and NRDA data needs could create conflicts in priorities for sample collection, possibly causing a delay in the reporting of operational effectiveness back to the Unified Area Command if both types of data are being collected from a single research vessel.

Despite these challenges, both documents provide a flexible framework for incident-specific monitoring plan development and recommend the type of data that should be collected. However, these plans are not a replacement for detailed shipboard Field Test Plans, which should be developed prior to an operational monitoring research cruise. With limited time to deploy this type of field monitoring in the early hours of a spill response involving dispersants, it is essential that the operational monitoring protocols are standardized to ensure that the three main objectives of dispersant operational monitoring are achieved:

Objective 1: Confirmation of dispersant effectiveness under present spill conditions; for example, meteorology and (physical) oceanography conditions, oil type, weathering state, particulate matter, and marine snow production.

Objective 2: Initial field screening characterization of the dispersed oil concentrations at depths within the water column. These data can be very useful in calculating toxic units and therefore characterizing toxicity (as explained in Chapter 3).

Objective 3: Detailed laboratory chemical characterizing of relevant water samples, which allows decision makers to refine estimates on potential toxicity or other biological effects that may have occurred.

Proper field protocols are essential to ensure:

- safe deployment of the research team and equipment;
- proper use of field equipment;
- consistent field sample collection, preparation and analysis; and
- accurate, timely reporting across multiple research vessels back to the decision makers within the Unified Area Command.

Capturing these field protocols in a comprehensive shipboard research plan that is available for deployment prior to an incident occurring is essential. Important information for inclusion in the plan includes:

- minimum required training for all shipboard research personnel;
- shipboard cruise hazards identification;
- safety data sheets for all chemical components used on board;
- Occupational Safety and Health Administration monitoring requirements for inhalation of volatile organic compounds (e.g., real-time BTEX detection);
- required field collection permits;
- proper manufacturer instructions for operation of all scientific equipment;
- sample handling, labeling, and chain of custody procedures;
- weather contingencies; and
- prioritization of all sampling because there will be times when not all parameters can be sampled for various reasons. The team needs to know what samples and parameters to give the highest priority to in order to reach the overarching goals of the sampling mission.

Emerging Issues and Advances

Rapid Field Screening for Hydrocarbons

One of the challenges with meeting Objective 2 (initial field screening of hydrocarbons) is the reliance on traditional analytical methods such as gas chromatography coupled to either flame ionization detection (GC-FID) or mass spectrometry (GC-MS). During the DWH spill response, tens of thousands of water samples were collected and shipped to analytical laboratory laboratories across the United States for later analysis (OSAT, 2010). Laboratories were inundated, and some samples were not analyzed until long after the spill response had ended. A review of chemistry reports indicates that many of those backlogged samples contained no detectable petroleum compounds (OSAT, 2010). These delays posed challenges for the Unified Area Command, as they lacked information that could inform ongoing response operations.

The implementation of rapid field screening protocols could minimize the “bottleneck effect” of backlogged samples in the future. The use of rapid screening methods is not new, with early publications on this topic dating back to the mid-1990s (Owens and Sergy, 1997). Since that time, several new technologies have debuted that would enable shipboard personnel to conduct rapid screening of water samples to help focus the collection of samples for Objective 3 (detailed laboratory chemical characterization). If rapid field monitoring could eliminate locations or water depths where “non-detects” are observed, collection of relevant samples of oil and dispersed oil could be more strategic. In other words, collect relevant samples via use of “quick screening” to determine where sample collection should be focused. Several portable hydrocarbon analyzers and handheld gas chromatography flame ionization detectors are available that could effectively meet Objective 2, while also optimizing sampling strategies for Objective 3.

During DWH, BP was directed to develop and implement a water column monitoring program that included shipboard toxicity testing. However, it is difficult to conduct shipboard toxicity testing due to logistical requirements such as space availability, temperature control, animal culturing, stability, exposure to ship exhaust, and time requirements. Many organisms are very sensitive and cannot withstand the physical turbulence of shipboard testing, and even the most rapid tests require a 24-hour incubation period. The Rotox M kit (MicroBio Tests, Inc.), utilizing rotifers as the test organism, was selected to meet these criteria because it is commercially available, requires very little space or special equipment, has no feeding requirement, and can withstand unfavorable conditions at sea. A review of 1,242 samples (1,047 collected samples, 195 controls) indicated that only 26 samples had mortality greater than 20% (22 collected field samples and 4 controls). Most of the mortality corresponded to adverse weather and/or poor lab conditions which increased the physical trauma to the organisms being tested (OSAT, 2010). There is no evidence that shipboard toxicity testing yielded any actionable information for the decision makers within the Unified Command. Instead, implementation of a “quick screening” protocol for collecting hydrocarbon data for use in a toxicity model to generate toxic units would yield useful information to support ongoing dispersant operations.

FINDINGS AND RECOMMENDATIONS

Finding: Great strides have been made in the quantification of petroleum- and dispersant-related compounds, but there is a gap between this technology development and subsequent application to oil spills.

Recommendation: Relevant federal authorities, including the National Oceanic and Atmospheric Administration (NOAA) and the U.S. Coast Guard (USCG), should track emerging technologies and provide support and opportunities for those technologies to be tested for applicability to marine oil spill response. Promising technologies should be supported and brought to a state of application readiness, perhaps with support from industrial partners. Responsible agencies should further coordinate such analyses during a major spill, perhaps with input from the scientific community, so as to achieve additive benefit from complementary approaches.

Finding: The capacity to quantify discharge and dissolution from an aerial platform, as demonstrated during the *Deepwater Horizon* (DWH) oil spill, provides a powerful tool to the response community, which has since been applied to two additional blowout scenarios (the North Sea Elgin blowout and the Porter Ranch gas blowout). Despite proven utility and the potential of this tool to quantify dispersant efficacy during a blowout scenario, this capacity remains ad hoc and has not been funded as a response tool by relevant authorities.

Recommendation: Relevant response authorities, including NOAA and USCG, with support from industrial partners and other agencies, should formally incorporate and support aerial hydrocarbon quantification capabilities such as those demonstrated by Ryerson et al. (2011) as a flexible spill response tool to quantify discharge rate and transport processes.

Finding: Molecular tools as direct (culture-independent) techniques to determine microbial community structure, functional capabilities of the environment, stress responses, protein identity and abundance, and the relationship between specific organisms and substrate compounds have been advancing rapidly. This has been largely due to rapidly declining costs of these methods from many thousands of dollars to only a few dollars per sample. In addition, the speed at which analyses can be performed has decreased from months to hours. These techniques are also enabling an environmental systems biology approach to oil spills and the use of dispersants which will enable faster response times and better understanding at a systems level.

Recommendation: Molecular tools should be encouraged but only so long as the underlying assumptions of each assay is understood. Because these techniques can have biases, multiple assays and multiple lines of evidence are necessary to ensure that the conclusions from these techniques are correct. Developing detailed Field Sampling Plans with these molecular techniques and updating them on a regular basis with teams of experts is critical to avoid making incorrect conclusions about oil/dispersant efficacy for dispersion and bioremediation.

Finding: The understanding of the impacts of dispersant as a response tool has been greatly advanced by laboratory experiments and modeling, but these efforts are often limited by their inability to capture the complexity or scale found in the field. Important issues that are best answered in a field study or future spill (spill of opportunity) cover a broad spectrum of topics, including validation of integrated models and their sub-models, especially scaling of droplet size; better understanding of health impacts on response workers (unintentional releases only); validation of response decision-making approaches; and discovery of previously unknown linkages in complex ecosystems affected by oil.

Recommendation: Efforts to take detailed scientific measurements during future spills (spills of opportunity) and/or to conduct dedicated field experiments should be strongly encouraged. In the case of a spill of opportunity, preplanning and pre-deployment as well as focusing on the priorities for such observations are essential to avoid delays in the start of taking these measurements. Given its long-term funding and mandate, the National Academies Gulf Research Program,[8] or a foundation with similar long-term funding, would be in an ideal position to work with the Interagency Coordinating Committee on Oil Pollution Research to coordinate a field experiment or scientific efforts for deployment in a spill of opportunity.

Recommendation: Analyze the large quantity of available experimental toxicity data to investigate the question whether exposure media containing chemically dispersed oil is more toxic than is exposure media containing physically dispersed oil. The analysis would need to

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[8] As a result of settlements from the DWH spill, $500 million was designated to the development and 30-year endowment of the National Academies Gulf Research Program, whose mission is "catalyzing advances in science, practice, and capacity to generate long-term benefits for the Gulf of Mexico region and the Nation." In furtherance of its mission, the National Academies Gulf Research Program funds grants, fellowships, and activities.

include a quantitative estimate of the microdroplet concentration at each dilution, estimates of the dissolved concentrations, and the use of toxic units as the dose metric (see Chapter 3 for methods).

Finding: There are several limitations to methods used to assess human health effects of previous oil spills, making it difficult to determine causal relationships.

Recommendation: Establish and maintain baseline health metrics, readily available and deployable biomarkers of exposure and effect, and study protocols that are activated at the start of an oil spill for recruitment and collection of biospecimens from response workers and affected shoreline communities.

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APPENDIX A

COMMITTEE AND STAFF BIOGRAPHIES

COMMITTEE

Mary E. Landry (*Chair*) retired from the U.S. Coast Guard's (USCG's) Senior Executive Service in 2015 after more than 30 years of active duty with the USCG and the rank of Rear Admiral. Until 2015, RADM Landry served as the Senior Executive Director of Incident Management Preparedness Policy, where she was responsible for establishing, developing, and implementing all hazards incident management goals, strategies, policies, and doctrines to meet USCG responsibilities in incident preparedness and response. From May 2013 to May 2014, RADM Landry also served at the White House as the Special Assistant to the President and the Senior Director for Resilience Policy. During her flag service, RADM Landry served as the Commander of the Eighth Coast Guard District and the Commander of Task Force 189.8, based in New Orleans. In this role, she was responsible for USCG operations covering 26 states, more than 1,200 miles of coastline, and 10,300 miles of inland waterways. Moreover, RADM Landry served as the Federal On-Scene Coordinator in the *Deepwater Horizon* oil spill in 2010. She also held the position of Executive Officer of Marine Safety Office (MSO) Boston during the 9/11 attacks and oversaw the federal response to the Buzzard's Bay oil spill during her tour as the Commanding Officer of MSO Providence, Rhode Island. Her military decorations include the Legion of Merit (three awards), Meritorious Service Medal, Coast Guard Commendation Medal (three awards), 9-11 Medal, and Achievement Medal. Ms. Landry completed Officer Candidate School in 1980 after graduating from the State University of New York at Buffalo in 1978. She holds an MA in management from Webster University and a Master of Marine Affairs from the University of Rhode Island. She is also a National Security Fellow, earning this distinction at Harvard University's John F. Kennedy School of Government in 2000. Since retiring from the USCG, Ms. Landry currently serves as an Independent Corporate Director and as part of the Member Audit Committee for the United Services Automobile Association.

E. Eric Adams serves as a Senior Lecturer and a Senior Research Engineer in the Department of Civil and Environmental Engineering at the Massachusetts Institute of Technology (MIT). His areas of expertise include water quality modeling and the design and environmental evaluation of effluential disposal systems. Recent research projects include modeling multiphase plumes with application to deep-sea oil spills; applying chemical dispersants to subsurface oil spills; and creating a flexible curtain to contain oil from a deep ocean blowout. Dr. Adams is a member of both the American Society of Civil Engineering and the International Association of Hydro-Environment and Research. After receiving a BS in engineering from Harvey Mudd College, Dr. Adams went on to MIT to earn an SM in civil engineering and a PhD in hydrodynamics.

Adriana C. Bejarano is the Senior Aquatic Eco-Toxicologist at Research Planning, Inc. (RPI) in Columbia, South Carolina. Her past research includes the ecological and toxicological effects of organic pollutants on marine and estuarine invertebrates, and she has developed skills in applied ecology, modeling, ecological risk assessments of contaminated sediments and complex contaminant mixtures, and statistical data analysis. During her time at RPI, Dr. Bejarano has provided technical and scientific support to various inland and marine oil spills. She also led data analyses on the potential toxicological impacts of surface dispersant use to aquatic organisms during the *Deepwater Horizon* oil spill and co-authored a report to the U.S. Coast Guard. She also was the lead toxicologist of the Biological Assessment for the RRT4 and RRT9 Preauthorization Plan for Dispersant Use. Furthermore, Dr. Bejarano is an Adjunct Professor at the Department of Environmental Health and Sciences at the University of South Carolina and an active member of the Society of Environmental Toxicology and Chemistry. She received her PhD in aquatic toxicology from the Arnold School of Public Health at the University of South Carolina in 2004.

Michel Boufadel is a Professor of Environmental Engineering and the Director of the Center for Natural Resources Development and Protection at the New Jersey Institute of Technology. He also holds the title of Professor in the Department of Biological, Chemical, and Pharmaceutical Engineering. He is a professional engineer in New Jersey and Pennsylvania and a Fellow of the American Society of Civil Engineers. His expertise lies in environmental fluid mechanics and modeling of processes, and since 1995 he has applied that expertise in researching the behavior of oil. Dr. Boufadel was involved in addressing the persistence of the *Exxon Valdez* oil spill, the fate and behavior of the *Deepwater Horizon* oil spill, and the Enbridge Pipe 6 oil spill in Michigan. He has served on several National Academies of Sciences, Engineering, and Medicine committees dealing with oil spills. He also served on the Royal Society of Canada Committee on the Behaviour of Oil in Aqueous Environments, in 2016 and the U.S. Environmental Protection Agency Science Advisory Board on Shale Gas. He has more than 150 refereed publications in environmental fluid mechanics and modeling. He received a BS in civil engineering from the Jesuit University at Beirut in Lebanon, and an MS and a PhD in environmental engineering from the University of Cincinnati.

Gina Coelho has more than 25 years of experience in environmental research, consulting, program management, and regulatory compliance in the offshore oil and gas sector. She began working in the field of dispersant and dispersed oil research as a staff scientist for the Marine Spill Response Corporation (1993-1995). In 1996, she began working as an environmental consultant with a small firm supporting onshore and offshore oil and gas and related energy sector projects. Since that time, she has worked on projects for oil companies and associated regulatory agencies (including the U.S. Coast Guard, the U.S. Environmental Protection Agency, the Bureau of Ocean Energy Management, and the National Oceanic and Atmospheric Administration) on the use of science in supporting dispersant use, policy, and decision making. Dr. Coelho focuses on integrating dispersant and dispersed oil research into spill contingsency planning, and she serves as an expert on regulatory outreach and community engagement strategies on dispersant issues, both in the United States and abroad. She previously served as the President of Ecosystem Management & Associates, Inc., and as a Principal Professional Associate and the Offshore Oil and Gas Sector Director for HDR Inc. Most recently, she worked as a Principal Senior Scientist for Sponson Group, Inc. Dr. Coelho was the Chief Scientist on the *Deepwater Horizon* oil spill monitoring of subsea dispersant injection, and she served as a scientific liaison between BP and the trustees on dispersant issues during and after the spill response. In addition, she has worked on other spills in U.S. waters. She received a BA in biology from St. Mary's College of Maryland, completed her graduate coursework through the University of Maryland Chesapeake Biological Laboratory, and received her PhD in ecology/environmental science from Bircham International University in Madrid, Spain.

Thomas S. Coolbaugh is an Oil Spill Response Advisor for Exxon Mobil Corporation's Safety, Security, Health and Environment Support organization where he provides technical guidance and training on the full suite of oil spill response strategies in support of global operations. Dr. Coolbaugh has extensive experience in a variety of research settings as a scientist and leader. He is a Vice Chair of IPIECA's (formerly the International Petroleum Industry Environmental Conservation Association) Oil Spill Working Group (immediate past Chair) as well as a member of the American Petroleum Industry Spills Advisory Group; the Marine Preservation Association Dispersant Advisory Committee; and the Science Advisory Panel of the University of New Hampshire/National Oceanic and Atmospheric Administration Coastal Response Research Center. He served on the National Research Council's Committee on Responding to Oil Spills in the U.S. Arctic Marine Environment and was an invited subject-matter expert for a Consensus Environmental Risk Assessment project led by the U.S. Coast Guard Sector Delaware Bay relating to potential incidents involving Bakken crude and diluted bitumen. His focus is often on the scientific understanding and regulatory aspects of the use of dispersants during an oil spill response and communicating with a variety of groups on the topics. Dr. Coolbaugh received his BA in chemistry from Amherst College, a PhD in chemistry from the California Institute of Technology (Advisor: Professor Robert Grubbs, 2005 Nobel Laureate), and an MS in the management of technology from New York University. He has been with ExxonMobil since 1988.

Cortis Cooper retired after more than 27 years of service as a Fellow with the Chevron Energy Technology Company, 1 of 22 Chevron scientists who advise corporate managers about science-related issues. Over his career in the offshore industry, he has focused on quantifying winds, waves, and currents that are used by engineers to operate and design offshore facilities at various locations around the world. His research has included the study of the fate of oil spills; modeling hurricane alleys in the Gulf of Mexico; forecasting the Loop Current and associated eddies in the Gulf of Mexico; supervising the development of ocean current models in the Gulf of Mexico; and investigating the fate of oil and gas from deepwater blowouts. Dr. Cooper was a member of the National Research Council's Committee on Oil in the Sea: Inputs, Fates, and Effects, and he formerly served as a member of the Ocean Studies Board. He earned a BS in civil engineering and an MS from the Massachusetts Institute of Technology and a PhD in environmental engineering from the University of Maine.

Dominic M. Di Toro (NAE) is the Edward C. Davis Professor of Civil and Environmental Engineering in the Department of Civil and Environmental Engineering at the University of Delaware. He has specialized in the development and application of mathematical and statistical models to stream, lake, estuarine, and coastal water as well as to sediment quality problems. He has participated in the development of water and sediment quality criteria for the U.S. Environmental Protection Agency; sediment flux models for nutrients and metals; and integrated hydrodynamic, sediment transport, and water quality models. Recently he has participated in developing models for predicting environmental partitioning and toxicity parameters from molecular structure. He is a member of the National Academy of Engineering and served on the National Research Council's

Committee on Sediment Dredging at Superfund Megasites and the Committee on the Evaluation of Chesapeake Bay Program Implementation for Nutrient Reduction to Improve Water Quality. He received a BEE from Manhattan College, and both an MA in electrical engineering and a PhD in civil and geological engineering from Princeton University.

Julia M. Gohlke is an Associate Professor in the Department of Population Health Sciences at Virginia Polytechnic Institute and State University. Her research utilizes spatial epidemiology, risk assessment, and toxicology approaches to characterize human health implications of global environmental change and large-scale environmental disasters, including the *Deepwater Horizon* blowout. She has served on several advisory boards related to environmental health, including for federal agencies such as the U.S. Environmental Protection Agency, the National Institute of Environmental Health Sciences, and the Centers for Disease Control and Prevention. She received a BS in biology at the University of Michigan and both an MS and a PhD in environmental health at the University of Washington.

Bernard D. Goldstein (NAM) is the Emeritus Dean and an Emeritus Professor of Environmental and Occupational Health at the University of Pittsburgh Graduate School of Public Health. He is an elected member of the National Academy of Medicine, and he has chaired more than a dozen National Research Council and National Academies of Sciences, Engineering, and Medicine committees. He has also chaired committees related to environmental health for the World Health Organization and the United Nations Environment Programme. His past experience includes service as Assistant Administrator for Research and Development of the U.S. Environmental Protection Agency, 1983-1985, and President of the Society for Risk Analysis. His involvement in the *Deepwater Horizon* oil spill includes serving as an Advisory Board member of the National Academies Gulf Research Program and as the original chair of the Coordinating Committee of the Gulf Research Health Outreach Program. He is also active on shale gas issues and on issues related to the science/policy interface.

Terry C. Hazen currently holds a joint appointment with the University of Tennessee–Knoxville's College of Engineering's Civil and Environmental Engineering Department and the College of Arts and Sciences' Microbiology and Earth and Planetary Sciences Departments. He also serves as a Faculty Fellow at the University of Tennessee–Oak Ridge National Laboratory's Joint Institute for Biological Sciences and the Center for Environmental Biotechnology. Specializing in bioremediation and bioenergy, Dr. Hazen focuses his research more narrowly on how naturally occurring bacteria can sometimes break down and detoxify hazardous material. He also works with a team of researchers who have developed a method of using bacteria to help test for the presence of a wide array of pollutants. He previously served as the Program Director for the *Deepwater Horizon* Oil Spill Systems Biology program at the Energy Biosciences Institute at the University of California, Berkeley. Dr. Hazen received both a BS and an MS in interdepartmental biology, specializing in parasitology, from Michigan State University and a PhD in parasitology-ecology from Wake Forest University.

Kenneth Lee is the National Senior Science Advisor for Oil Spill Research, Preparedness and Response for Fisheries and Oceans Canada. Until recently he was the Director of Oceans and Atmosphere in the Commonwealth Scientific and Industrial Research Organisation (Australia's national science agency) with the goal to enhance Australia's prosperity and well-being through research to underpin sustainable economic, social, and environmental use of Australia's marine estate and the management of its atmospheric environment. He also served on the Australian Government's National Plan for Maritime Environmental Emergencies Committee. Dr. Lee's research activities include studies on the transport, biotransformation, and biodegradation of organic and inorganic contaminants; development of toxicological and modeling approaches to assess the potential impact of the offshore oil and gas industry (including accidental oil spills); and the development and validation of oil spill countermeasure technologies. He served on the National Research Council's Committee on the Effects of the *Deepwater Horizon* Mississippi Canyon-252 Oil Spill on Ecosystem Services in the Gulf of Mexico and the Committee on Arctic Oil Spill Response. In 2016, Dr. Lee chaired the Royal Society of Canada's Expert Panel on the The Behaviour and Environmental Impacts of Crude Oil Released into Aqueous Environments. Dr. Lee received a BSc in biology from Dalhousie University, and both an MSc and a PhD in botany/environmental studies from the University of Toronto.

Steven A. Murawski is a Professor and the Peter Betzer Endowed Chair of Biological Oceanography in the College of Marine Science at the University of South Florida. His research group aims to understand the impacts of human activities on the sustainability of ocean ecosystems. He has developed approaches for understanding the impacts of fishing on marine fish complexes exploited in mixed-species aggregations, with the goal to help inform investments to rebuild the Gulf of Mexico from effects of the *Deepwater Horizon* oil spill, loss of nursery areas, nutrient enrichment, and overfishing. Dr. Murawski serves as Director of the Center for Integrated Analysis and Modeling of Gulf Ecosystems, is a U.S. Delegate of the International Council for the Exploration of the Sea, and is a member of the National Academies of Sciences, Engineering, and Medicine's Ocean Studies Board, in addition to being appointed to serve on the Committee for Decadal Survey of Ocean Sciences 2015. He received a BS and an MS in fisheries biology and a PhD in fisheries and wildlife biology from the University of Massachusetts Amherst.

W. Scott Pegau is a Research Scientist and a Research Program Manager at the Oil Spill Recovery Institute (OSRI). His research aims to develop novel oil spill detection and tracking approaches to understand the fate and behavior of oil spilled in the Arctic and sub-Arctic. At OSRI, he monitors grant contracts and provides leadership in planning research programs. Prior to joining OSRI, Dr. Pegau was a Senior Scientist and a Research Coordinator at the Kachemak Bay Research Reserve in Alaska. He received a BS in physics from the University of Alaska Fairbanks and a PhD in oceanography from Oregon State University.

Ronald Tjeerdema is the Associate Dean of Environmental Sciences and the Donald G. Crosby Endowed Chair in Environmental Chemistry at the University of California, Davis. With a focus on marine and freshwater ecosystems, Dr. Tjeerdema's areas of expertise range from chemical fate in the environment, sensitive life stage bioassays, and biochemical mechanisms of toxicity. He also has worked extensively with pesticides, petroleum hydrocarbons, dispersants, and marine algal toxins. Notably, his research on oil spills and dispersants resulted in the development of the widely used standardized Chemical Response to Oil Spills: Ecological Research Forum methods for toxicity assessment. During the aftermath of the *Deepwater Horizon* oil spill, Dr. Tjeerdema served on several National Oceanic and Atmospheric Administration panels advising on response plans. He currently serves as co-Editor-in-Chief on the flagship journal *Aquatic Toxicology.* He completed his PhD in pharmacology and toxicology, with an emphasis on environmental toxicology, in 1987 from the University of California, Davis.

David L. Valentine is a Professor of Geochemistry and Microbiology and holds the Norris Presidential Chair in Earth Science at the University of California, Santa Barbara. His main research interest is the interactions of microbes and the Earth system and, more specifically, the Archaea, biogeochemistry, and microbial ecology of hydrocarbons and the development of novel isotopic approaches to study microbes and geochemical processes. Dr. Valentine's lab currently works on projects probing the global methane and hydrogen cycles, with field sites from Alaska to the Coal Oil Point seep field in California. He is well known for his contributions to understanding the fate of hydrocarbons and bacteria from the *Deepwater Horizon* oil spill. He was the recipient of the National Science Foundation CAREER award and is a fellow of the Aldo Leopold Leadership Program. After receiving a BS and an MS in chemistry from the University of California, San Diego, Dr. Valentine went on to earn another MS and a PhD in earth system sciences from the University of California, Irvine.

Helen K. White is an Associate Professor of Chemistry and Environmental Studies at Haverford College in Haverford, Pennsylvania. Dr. White's research interests examine the sources, sinks, and cycling of human-derived compounds in the marine environment with a focus on how chemical structure, physical associations, and bioavailability determine the persistence of specific organic compounds. Dr. White has investigated persistent oil residues in the Gulf of Mexico following the *Deepwater Horizon* oil spill as well as in Prince William Sound, Alaska. Dr. White is a recipient of the National Academies of Sciences, Engineering, and Medicine's Gulf Research Program's Early-Career Fellowship and a Henry Dreyfus Teacher-Scholar Award. Dr. White received her MChem in chemistry from the University of Sussex, United Kingdom, and her PhD in chemical oceanography from the Massachusetts Institute of Technology and the Woods Hole Oceanographic Institution. Following her graduate studies, Dr. White was awarded the Microbial Science Initiative Postdoctoral Fellowship at Harvard University.

STAFF

Susan Roberts is the Director of the Ocean Studies Board at the National Academies of Sciences, Engineering, and Medicine. She started as a Program Officer for the Ocean Studies Board in 1998 and became the Director of the Board in 2004. Dr. Roberts specializes in the science and management of living marine resources. She has served as the Study Director for 18 reports produced by the National Academies on topics covering a broad range of ocean science, marine resource management, and science policy issues. Her research publications include studies on fish physiology and biochemistry, marine bacterial symbioses, and cell and developmental biology. Dr. Roberts received her PhD in marine biology from the Scripps Institution of Oceanography. Prior to her position at the Ocean Studies Board, she worked as a postdoctoral researcher at the University of California, Berkeley, and as a senior staff fellow at the National Institutes of Health. Recently, she served on the editorial panel for the United Nations Educational, Scientific and Cultural Organization's Intergovernmental Oceanographic Commission Global Ocean Science Report (2017) and currently is a member of the editorial panel for the second edition. Dr. Roberts is an elected Fellow of the American Association for the Advancement of Science and the Washington Academy of Sciences.

Stacee Karras is a Program Officer with the Ocean Studies Board. She joined the National Academies of Sciences, Engineering, and Medicine in 2012 as a Fellow and served as a Research Associate for the Ocean Studies Board between 2013 and 2015. She then served as an Associate Program Officer until 2016, when she took on her current role. She received both a BA in marine affairs and policy (with concentrations in biology and political science) and an MA in marine affairs and policy from the University of Miami—the latter from the university's Rosenstiel School of Marine and Atmospheric Science. She earned her JD from the University of Virginia's School of Law.

Trent Cummings received a BA in environmental studies/sustainability from The George Washington University in Washington, DC. Prior to working at the National Academies of Sciences, Engineering, and Medicine, he interned with the Business Network for Offshore Wind covering the completion of the Block Island Wind Farm. He joined the Ocean Studies Board as a program assistant in December 2017.

APPENDIX B

DISCLOSURE OF UNAVOIDABLE CONFLICT OF INTEREST

The conflict-of-interest policy of the National Academies of Sciences, Engineering, and Medicine (www.nationalacademies.org/coi) prohibits the appointment of an individual to a committee like the one that authored this Consensus Study Report if the individual has a conflict of interest that is relevant to the task to be performed. An exception to this prohibition is permitted only if the National Academies determine that the conflict is unavoidable and the conflict is promptly and publicly disclosed.

When the committee that authored this Consensus Study Report was established a determination of whether there was a conflict of interest was made for each committee member given the individual's circumstances and the task being undertaken by the committee. A determination that an individual has a conflict of interest is not an assessment of that individual's actual behavior or character or ability to act objectively despite the conflicting interest.

Dr. Thomas S. Coolbaugh was determined to have a conflict of interest because he is employed by ExxonMobil Research and Engineering Company, whose financial interests could be affected by the outcome of the study.

The National Academies determined that the experience and expertise of the individual was needed for the committee to accomplish the task for which it was established. The National Academies could not find another available individual with the equivalent experience and expertise who did not have a conflict of interest. Therefore, the National Academies concluded that the conflict was unavoidable and publicly disclosed it through the National Academies Current Projects System (https://nationalacademies.org/pa).

APPENDIX C

ACRONYMS AND ABBREVIATIONS

ACR	acute-to-chronic ratio
ADIOS2	Automated Data Inquiry for Oil Spills version 2
API	American Petroleum Institute
BaPE	benzo[*a*]pyrene equivalents
BOP	blowout preventer
BSEE	Bureau of Safety and Environmental Enforcement
BTEX	benzene, toluene, ethylbenzene, and xylene
BW	body weight
CAFE	Chemical Aquatic Fate and Effects
CDC	Centers for Disease Control and Prevention
CERA	Consensus Ecological Risk Assessment
CEWAF	chemically enhanced water-accommodated fraction
CF	conversion factor
CI	confidence interval
CR	consumption rate
CRA	Comparative Risk Assessment
CROSERF	Chemical Response to Oil Spills: Ecological Effects Research Forum
CSF	cancer slope factor
DFO	Fisheries and Oceans Canada (Department of Fisheries and Oceans)
DIVER	Data Integration Visualization Exploration and Reporting
DOR	dispersant-to-oil ratio
DOSS	dioctyl sodium sulfosuccinate
DS	model proposed by Delvigne & Sweeney or DeepSpill
DSD	droplet size distribution
DWH	*Deepwater Horizon*

ED	exposure duration
EIS	Environmental Impact Statement
EL50	median effects-loading concentration
EPA	U.S. Environmental Protection Agency
EPS	extracellular polymeric substance
EqP	equilibrium partitioning
ERL	effects range low
ES	ecosystem services
ESA	ecosystem services analysis
FDA	U.S. Food and Drug Administration
FEV	forced expiratory volume
FVC	forced vital capacity
GC	gas chromatography
GC-FID	gas chromatography and flame ionization detection
GC-MS	gas chromatography and mass spectrometry
GDS	Global Dispersant Stockpile
GNOME	General NOAA (National Oceanic and Atmospheric Administration) Operational Modeling Environment
GoMRI	Gulf of Mexico Research Initiative
GOR	gas-to-oil ratio
GRIIDC	Gulf of Mexico Research Initiative Information & Data Cooperative
HC5	hazard concentration 5%
HEWAF	high-energy water-accommodated fraction
HYCOM	Hybrid Coordinate Ocean Model
IDLH	Immediately Dangerous to Life or Health
IFT	interfacial tension
IOGP	International Association of Oil & Gas Producers
IRB	Institutional Review Board
ISB	in situ burning
IVOC	intermediate-volatility organic compound
LC50	median lethal concentration
LEWAF	low energy water-accommodated fraction
LISST	Laser In Situ Scattering and Transmissiometry
LL50	lethal loading 50
LN	log-normal
LOC	level of concern
LT50	lethal time 50
MAH	monoaromatic hydrocarbon
MD	microdroplet concentration
MEWAF	medium-energy water-accommodated fraction
MEXUS	Mexico–United States
MOS	marine oil snow
MOSSFA	Marine Oil Snow Sedimentation and Flocculent Accumulation

MPa	megapascal
MS	mass spectrometry
NAPL	non-aqueous-phase liquid
NEBA	Net Environmental Benefit Analysis
NIEHS	National Institute of Environmental Health Sciences
NIOSH	National Institute for Occupational Safety and Health
NMFS	National Marine Fisheries Service
NOAA	National Oceanic and Atmospheric Administration
NRC	National Research Council
NRDA	Natural Resource Damage Assessment
NRT	National Response Team
OMA	oil-mineral aggregate
OPA	oil-particle aggregate
ORMS	oil-related marine snow
OSHA	Occupational Safety and Health Administration
PAH	polycyclic aromatic hydrocarbon
PDMS	polydimethylsiloxane
PLC50	median phototoxic lethal concentration
PPE	personal protective equipment
PTSD	posttraumatic stress disorder
RANS	Reynolds-Averaged Navier-Stokes
RfD	reference dose
RL	risk level
ROC	resource of concern
SABGOM	South Atlantic Bight—Gulf of Mexico
SilCam	silhouette camera
SIMA	Spill Impact Mitigation Assessment
SOA	secondary organic aerosol
SOO	spill of opportunity
SPME	solid-phase microextraction
SSD	Species Sensitivity Distribution
SSDI	subsea dispersant injection
SVOC	semi-volatile organic compound
SwRI	Southwest Research Institute
TAMOC	Texas A&M Oilspill Calculator
THC	total hydrocarbon concentration
TLM	target lipid model
TPAH	total polycyclic aromatic hydrocarbon
TPH	total petroleum hydrocarbon
TROPICS	Tropical Oil Pollution Investigations in Coastal Systems
TU	toxic unit
TUHH	Hamburg University of Technology

UI	uncertainty interval
UNCLOS	United Nations Convention on the Law of the Sea
USCG	U.S. Coast Guard
UV	ultraviolet
VEC	valued ecosystem component
VOC	volatile organic compound
WAF	water-accommodated fraction

APPENDIX D

MINORITY REPORT

Assessment of Uncertainty in Droplet Size Models and Its Impact on Calculated Oil Fate

By Cortis Cooper and Eric Adams

BACKGROUND

Task 6 of the committee's Statement of Task calls for an assessment of the adequacy of the existing information (tools) to support risk-based decision making. The intent of the discussion below is to assess the uncertainty of the droplet size estimates made by five published models. Published work does not provide the type of assessment needed to satisfy Task 6. To satisfy Task 6, one needs to compare the models with a wide range of observations. Some limited comparisons have been done by most of the model authors but as described below these are frequently limited or flawed. Given these factors and the several hundred high quality laboratory observations made since *Deepwater Horizon* (DWH), a more detailed comparison by a neutral party is called for.

In our comparisons we use some observations that have not yet been published in peer-reviewed journals though they are thoroughly documented in detailed technical reports made publicly available for several years (Brandvik et al., 2014, 2017). These observations also use the same techniques utilized in the observations that have been widely used by the modelers in their published comparisons (Brandvik et al., 2013, 2018, 2019a,b). A review of the unpublished reports shows numerous replicates with demonstrable repeatability. We use some of these replicates to show that committee concerns about possible fractionation in the Brandvik et al. (2017) dataset are unsubstantiated.

The additional analysis described below has not been published but there is a long history of similar analysis done in National Research Council reports (e.g., estimates of the single-most important source of oil in the sea were developed by the Committee on Oil in the Sea: Inputs, Fates, and Effects [NRC, 2003]). As in that report, we have provided the details and references that would be needed to reproduce our results. Finally, we are not attempting to choose a "winning" droplet model but rather to better quantify the uncertainty of the existing droplet models and then, most importantly, to understand how that uncertainty propagates into the oil fates calculated by an integrated model.

As stated above, previous assessment of droplet model accuracy has been done by the authors of the respective models but it has often been limited in scope or used flawed methods for validation.

For example, Oildroplets (Nissanka and Yapa, 2017b) was compared against only 11 observations and VDROP-J to 9 oil jet experiments (Zhao et al., 2014). ASA's model (Li et al., 2017) did a similar number of comparisons with oil jets. Paris et al. (2012) used the model of Boxall et al. (2012), who did many experiments but utilized a stirred reactor, not oil jetting into water. SINTEF's model (Johansen et al., 2013) was originally compared against 8 observations but 1 year later the calibration coefficients were adjusted using 14 more experiments (Brandvik et al., 2018). These coefficients compared well to subsequent experiments (Brandvik et al., 2014, 2017, 2019a) though recently the A coefficient was slightly modified to better fit measurements with live oil (Brandvik et al., 2019b). Further refinements have been made in the calculation of oil properties and in the droplet size distribution to account for large flow rates (Skancke et al., 2016).

With that in mind, we have reviewed the available observations and identified roughly 80 of them that were deemed of high quality and non-redundant. We then proceeded to program the three equilibrium models (SINTEF, ASA, and Paris) and compare them to these observations. We would have liked to do a similar comparison for the two population models, VDROP-J and Oildroplets, but their authors were unwilling to participate. Given the complexity of those models and our time constraints we could not include them. Nevertheless, we have been able to get some insights by examining published values for DeepSpill and DWH.

The next section compares the three equilibrium models to lab experiments and the DeepSpill experiment. It is followed by a look at DWH. The fourth section provides a summary followed by our conclusions. The last section is basically an appendix that briefly describes the laboratory observations used in our comparisons with special attention to the measurements of Brandvik et al. (2017) because these are so useful in testing the models at larger scale.

COMPARISON BETWEEN MODELS AND EXPERIMENTS

Figure D.1 compares three of the equilibrium models to the 80 experimental observations described in the last section. The figure shows that the Paris et al. (2012) model (green) underestimates droplet sizes by several orders of magnitude—consistent with the findings of Adams et al. (2013). The models of SINTEF and ASA show good predictive ability with a correlation coefficient squared of about 0.98. Both models are biased slightly low (model averages 2%-3% lower than observations). The average absolute percentage difference between model and observation for the SINTEF (Li) model is 24% (35%) with 90% confidence limits of roughly 50% (70%). However, a look at Figure D.1 shows that at times there are sizeable errors, which is reflected in the high coefficient of variation (mean/standard deviation) of ~1 for both models. These statistics become meaningless for the Paris model because predictions are an order of magnitude or more smaller than the observations.

Of particular interest is the DeepSpill field measurement (heart symbol) because it comes closest to DWH-like scales. The SINTEF model overestimates the observations by about 50% while the ASA model makes a perfect forecast. However, this perfection comes as no accident because ASA used the DeepSpill measurement to fit their model coefficients. Paris underpredicts by two orders of magnitude following the trend seen in Figure D.1 for the lab experiments. VDROP-J and Oildroplets have also been compared to DeepSpill in their respective publications and those are shown in row 2 of Table D.1.

The DeepSpill comparison for VDROP-J comes from Zhao et al. (2014) and is marked as questionable. That is because a careful reading of their paper shows that they used an optimized calibration coefficient, Kb, to calculate the 4,500 μm value. In a practical application of the model they would not be able to use an optimized fit but would have to use their Equation 33 to calculate Kb. How much difference would it make if they had used the predicted Kb instead of the best fit?

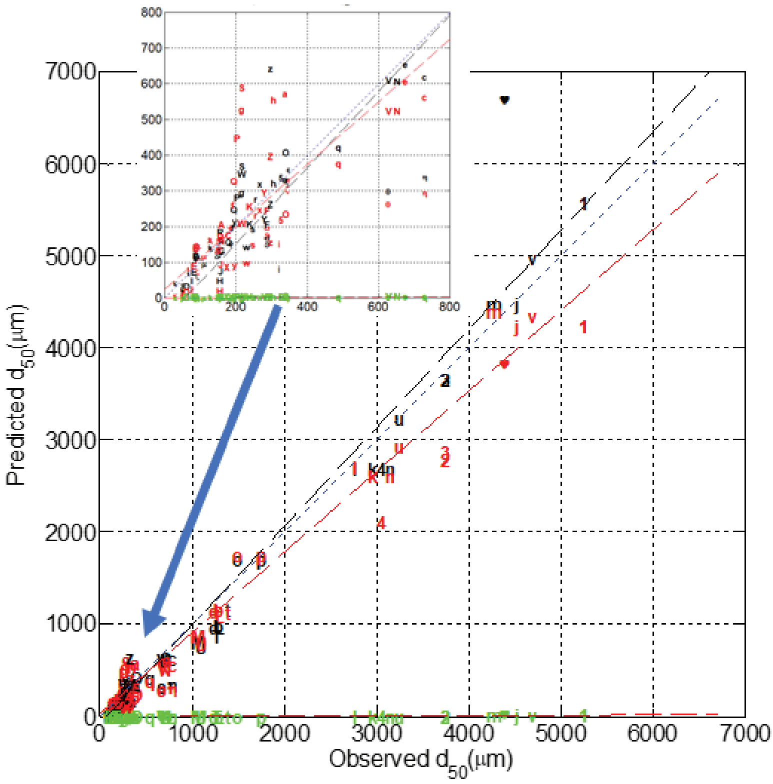

FIGURE D.1 Predicted versus observed d_{50} from three models: SINTEF (black), ASA (red), and Paris (green). Most of the Paris model predictions are less than 1 µm.

We do not know for sure without running the model again, but we can get a sense of its importance from their Figure 10 which suggests d_{50} = 0.5 mm, or nearly an order of magnitude less than their estimate using the best-fit Kb.[1] This estimate assumes linear extrapolation which is arguable but is taken here to show that the d_{50} calculated from VDROP-J is quite sensitive to Kb. If VDROP-J were re-run with the predicted Kb from Equation 33 it would predict a d_{50} substantially smaller than observed; hence the question mark in Table D.1.

Zhao et al. (2014) used best-fit Kb's when comparing VDROP-J to all the observations in their paper (see their Figures 6 to 13). This was a necessary first step to calibrate Kb and develop Equation 33. However, they never truly validated the predictive ability of the model by comparing it to a new set of observations using Equation 33. Though a less rigorous validation step, they could have at least compared the model to the calibration dataset using Equation 33 to calculate Kb. Had they done so they would have found the uncertainty bounds to be substantial given the sensitivity of VDROP-J's d_{50} estimate to variations in Kb (see DeepSpill example in previous paragraph) coupled with the considerable uncertainty in Equation 33 (see their Figure 14). It is noteworthy that Zhao et al. (2017a) and Nissanka and Yapa (2016) repeated this same process. In summary, the two population models have been calibrated, but not truly validated.

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[1] Equation 33 gives Kb = 0.100 using the properties listed in their Table 1. Figure 10 shows curves for three values of Kb. The curve for Kb = 0.028 shows a d_{50} = 5 mm while the curve for Kb = 0.05 gives a d_{50} = 3.5. Using these values and assuming linear extrapolation means a Kb = 0.10 gives d_{50} = 0.5 mm.

TABLE D.1 The d_{50} in μm Predicted by Models for Both Untreated and Treated Oil During *Deepwater Horizon* (DWH) and Untreated Oil During DeepSpill

Case	DOR%	SINTEF[a] Um	Spaulding[b]	ASA[c]	VDROP-J[d]	Paris um	Oildroplets
DeepSpill	0	6,700	NA	4,300	4,500?	32	~4,000
DWH	0	5,800	2,600	10,200	4,200	190	NA
DWH	0.4	1,800	100/2,600	3,400	1,300	70	NA
DWH	1.0	530	200/2,600	740	140	10	NA

[a] Calculated using ρ_o = 763 kg/m^3, μ = 0.7 cp, GOR = 0.4,3, σ = 24.5 cp (DOR = 0%), σ = 4.54 mN/m (0.4%), σ = 0.24mN/m (1%). Uses the SINTEF models described in Skancke et al. (2016) except that we have not accounted for temperature effects on oil viscosity.

[b] These are approximate peaks taken from Figure 9 of Spaulding et al. (2017). The 0.4% DOR case in the table comes from their "Best Estimate" while the 1% comes from their "high dispersant" case. The dual peaks in the droplet size distribution arise because they have assumed only partial mixing of the dispersant.

[c] These are estimates assuming oil characteristics at the surface as per Li et al. (2017). ρ_o = 862 kg/m^3, μ = 0.74 cp, GOR = 0.4, σ = 24.5 mN/m (DOR = 0%), σ = 4.54 mN/m (0.4%), σ = 0.24 mN/m (1%).

[d] From Gros et al., 2017.

COMPARISONS BETWEEN MODELS AND *DEEPWATER HORIZON* OBSERVATIONS

Table D.1 also compares the models for DWH cases with different dispersant-to-oil ratios (DORs). Unfortunately, there are no direct measures of droplet size but the work of Gros et al. (2017) suggests that a d_{50} of about 1 mm would satisfy their observed dataset, which corresponds to 0.4% DOR. This dataset is largely based on analyzed hydrocarbon concentration measurements integrated over time and space using the hydrocarbon fractionation methodology recommended in Chapter 5. By integrating over time and normalizing the concentration data by conservative constituents they remove many of the problems one runs into by comparing to raw time series. As shown in further runs by Socolofsky and Gros commissioned by this committee (henceforth referred to as SG and shown in Appendix E), their dataset is remarkably good at discriminating between proposed droplet sizes.

The third row of Table D.1 shows the case of 0.4% DOR and indicates that both VDROP-J and the SINTEF model fall close to the 1 mm value suggested by Gros et al., thus providing some validation for those models. The value from Spaulding et al. (2017) assumes a dual-peaked droplet size distribution for the dispersed cases based on their argument that the dispersant was not thoroughly mixed. The follow-on modeling by SG does not reproduce the Gros et al. dataset well. At 3.4 mm, the ASA model is considerably larger than 1 m but SG did not make a run with 3.4 mm so we cannot say for sure how it would compare to their dataset. However, the CRA-2 study described in Chapter 6 (see Figure 6.9a) does suggest that the difference between 1 and 3.4 mm would not substantially affect degradation, evaporation, or oil in the water column implying that the ASA estimate might not compare too badly to the Gros dataset.

Table D.1 shows that the Paris model predicts a d_{50} of 70 μm. SG ran a case with a d_{50} = 115 μm for DWH and found that virtually no oil made it to the surface, and far too much oil was found subsurface. In short, the Paris result is clearly inconsistent with the Gros et al. (2017) dataset and numerous other sources such as Ryerson et al. (2012) showing substantial oil at the surface.

One noteworthy point to make is that the two droplet models (VDROP-J and SINTEF, and arguably[2] ASA's model) replicate the Gros et al. dataset and do so without including some of the complicating processes conjectured in Chapter 2 (large pressure gradients, churn flow, or tip streaming). This suggests that those processes were not substantial for DWH. That is not to say that these processes could not be important in other scenarios.

In summary, both the VDROP-J and SINTEF models indicate a d_{50} that compares well with what we consider to be the best available estimate of the DWH d_{50} available to date inferred by Gros et al. (2017). The ASA model is a bit on the high side though it would likely still compare fairly well with the Gros dataset. On the other hand, the Paris d_{50} is too small by an order of magnitude.

Table D.1 also shows d_{50} values for a 0% and 1% DOR so it is interesting to compare VDROP-J, ASA, and SINTEF for these other values even though we do not have any observations for these cases from DWH. The ratios among the three models are remarkably constant at 0% and 0.4% DOR (i.e., the SINTEF model is 1.4× of the VDROP-J value while the ASA model is near 2.5). However, that trend stops at 1% DOR where these factors more than double. In other words, VDROP-J reduces the d_{50} at 1% far more than the other two models. Which model is correct? There are no observations to help us but it is worth noting that VDROP-J was calibrated with only two experiments where dispersant was applied (Zhao et al., 2014, 2017a). In contrast the SINTEF and ASA models have now been compared to 33 experiments in Figure D.1 with SSDI applied.

How much do the differences in predicted droplet size between the three models affect the calculated fate? For the 0% and 0.4% DOR, the answer is probably not much. This is based on the CRA-2 study described in Chapter 6. Figure 6.9a taken from that study shows that at 1,500 m there is little change in the volumes going to evaporation and degradation for droplets greater than 1 mm. However, at 1%, Figure 6.9a shows that there is a sizable difference. For example, the SINTEF (530 μm) and ASA models (740 μm) result in a degradation of 10%-15% of the total spill volume while VDROP-J (140 μm) is 40%-50%. In short, one walks away with a very different picture of SSDI effectiveness at 1% DOR if one uses VDROP-J instead of the others.

SUMMARY

Though the five droplet models mentioned in Chapter 2 have been compared to observations by their authors, all but the SINTEF model have considered a relatively small set of about a dozen oil jet experiments. There are now roughly 200 oil jet experiments available for comparisons, mostly from Brandvik et al. (2013, 2014, 2017, 2018, 2019a,b). These experiments cover a wide range of scales and conditions—discharge diameters of 0.5 to 50 mm and flow rates of 0.2 to 400 l/min, pressure ranges of 2 to 1,500 m of water, multiple DOR values, multiple oil densities, multiple gas-to-oil ratios (GORs), and live oils. Further details are given in the last section.

We selected 80 experiments from this large set of observations and compared three equilibrium models to those. These comparisons show that both the ASA and SINTEF models compare well with a correlation coefficient squared of about 0.98 though there is considerable scatter as indicated by 90% confidence limits of up to 70%. The Paris model underestimates the observations by orders of magnitude for reasons identified in Adams et al. (2013).

Some might argue that the good performance of the ASA and SINTEF model is because they have tuned their calibration coefficients to the observations. A close look at the sequence of publications of these models shows that they based their calibration coefficients on a dozen or so observations that did not include the vast majority of the measurements in our Figure D.1.

The authors of the two population models, VDROP-J and Oildroplets, were unwilling to participate in our comparison. Given the model complexity, we could not program them within our

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[2] The ASA d_{50} for 0.4% DOR is nearly three times larger than VDROP-J, so it could reproduce the Gros et al. (2017) dataset about as well as VDROP-J especially if one used a fairly large width parameter for the droplet size distribution.

time constraints. However, we were able to gather some insights about these models from published results for DeepSpill and DWH and further runs by SG.

Comparisons with the DeepSpill experiment reveal a number of important findings. First, the SINTEF model over-predicts the droplet size by about 50% though this is not too bad in light of the uncertainty in the observations. The Paris model predicts a droplet size two orders of magnitude too low. The ASA prediction is perfect but not insightful because they calibrated to the DeepSpill measurement. Finally, the authors of the two population models claim to closely match the DeepSpill experiment, but a close look at their comparisons reveals that they optimized their calibration coefficient to achieve that fit. If they had done a blind prediction, the error would have been larger. In the case of VDROP-J, we have done an estimate that suggests it would have underestimated the droplet size by a sizable amount.

Comparisons with the DWH dataset also gives some insights in several of the droplet models. Gros et al. (2017) and follow-on modeling by SG suggest the d_{50} for DWH was about 1 mm. Both the VDROP-J and SINTEF models predict roughly 1.5 mm while the ASA model predicts a value about two times larger. Unfortunately, SG did not run the ASA value but a look at the CRA-2 study suggests it might still compare reasonably well to the Gros dataset. The SG results show the Paris model prediction of 0.07 mm is far too small and that the dual-peaked droplet size distribution of Spaulding et al. (2017) compares less well than the VDROP-J and SINTEF models.

We also compared the models at two other DORs (0% and 1%) for the DWH conditions and found that VDROP-J gives a much smaller droplet size than the other two models at 1% DOR. There are no observations to check which model is correct but it is worrisome that VDROP-J was calibrated with only two observations that used dispersant. Because VDROP-J suggests such a substantial decrease in droplet size from 0% to 1% DOR, it makes SSDI look a lot more appealing than do the other two models.

Finally, we need to comment on the droplet size distribution. As pointed out in Chapter 2, the equilibrium models only predict the d_{50} and then use a heuristic method to calculate the droplet distribution. In contrast, the population models predict both the d_{50} and the distribution. Furthermore, the equilibrium models redistribute droplets in bin sizes greater than the largest stable droplet size using an ad hoc approach. The authors of the equilibrium models have spent little effort validating these assumptions so this is a topic that should be investigated more thoroughly. That said, it is reassuring to note that the sensitivity studies by French-McCay and Crowley (2018) show that the ultimate fate of the oil is fairly insensitive to the details of the size distribution. It is also reassuring that the SINTEF d_{50} compares so well to the experimental observations because in several of those cases the modeled d_{50} is shifted by as much as two times by their ad hoc method of dealing with droplets exceeding the maximum stable droplet size.

CONCLUSIONS

At last we are in a position to address Task 6 of the committee Work Scope with regard to droplet models. We conclude that both the ASA and SINTEF models probably can estimate droplet sizes with confidence limits of roughly 70% for simple jets. Given their firmer physical basis, VDROP-J and Oildroplets could perform even better but this is conjecture until these models are more thoroughly calibrated and truly validated using predicted calibration coefficients. It is reassuring that the VDROP-J and SINTEF models compare well with each other and the definitive DWH dataset of Gros et al. (2017). That said, it is troubling that VDROP-J suddenly breaks with the SINTEF and ASA models at a DOR of 1% and predicts a much smaller droplet size. This discrepancy is important because fate benefits will look far more positive with VDROP-J than with the other two models.

What are the implications of this uncertainty in the droplet models? Of course, we cannot answer that for a generic site but we can gain some insights for a large blowout by looking at the results of the CRA-2 study described in Chapter 6. Figure 6.9 shows the impact of droplet size on the peak volume of the oil during a blowout in a DWH-like setting. The upper panel applies to a site in 1,400 m of water while the lower panel is set in 500 m of water. For undispersed oil, one would expect a droplet size in the multi-mm range for a large blowout in either water depth. Using our confidence limit estimate of 70% and assuming d_{50} = 5 mm gives a range of 1.5-8.5 mm. Looking at the upper and lower panels of Figure 6.9, this range of d_{50} shows that the droplet uncertainty has negligible impact on the calculated fate in either water depth. These relatively big droplets rise so quickly to the surface that it really does not matter if they are 1 mm or 8 mm. On the other hand, for dispersed oil, a reasonable droplet size might be 0.5 mm, giving a range of 0.15-0.85 mm. Referring to Figure 6.9, we now see dramatically different fates at both 500 and 1,400 m depth. For example, in 1,400 m of water, roughly 50% of the oil mass ends up in the water column with d_{50} = 0.15 mm; it is about half that with d_{50} = 0.85 mm. While the CRA-2 focused on the Gulf of Mexico, the sensitivity to errors in droplet size will likely apply to many other parts of the world.

Based on this analysis we conclude:

1. The two equilibrium models from SINTEF and ASA predict 80 available observations from high-quality lab experiments with a mean error of less than 35% though with a fairly substantial scatter as reflected by the 90% confidence limits of 70%.
2. The published comparisons between observations and the two population models, VDROP-J and Oildroplets, are promising but inadequate because of their limited number and their use of calibration coefficients that were optimized to fit the individual experiments. Further comparisons are needed to truly validate the models for a wide range of conditions. Once this is done, the population models are likely to outperform the equilibrium models, in part because they predict both droplet and bubble sizes; the entire size distribution, not just the d_{50}; and the time evolution of the droplet/bubble sizes.
3. Comparisons with DWH suggest both the VDROP-J and SINTEF models predict reasonable droplet sizes though the uncertainty of the observed dataset remains a question mark as does the rather low d_{50} predicted by VDROP-J for the 1% DOR case.
4. The uncertainty in predicted d_{50} estimated in item 1 probably has little impact in calculating the droplet size for *untreated* oil in many high-volume blowout scenarios but that uncertainty can dramatically affect the modeled fate for *treated* (dispersed) oil. ***Hence, there is a demonstrable need for further research to remove uncertainty in droplet models especially for dispersed oil***.

SUPPLEMENTAL INFORMATION: DESCRIPTION OF EXPERIMENTAL OBSERVATIONS

Table D.2 summarizes the experiments used in the comparisons and the attached spreadsheet documents the key properties used as model input. The first column of the spreadsheet includes a “symbol” that can be used to trace that particular experiment to Figure D.1. All of the experiments involved jetting of oil into seawater though some also included methane either as free gas or saturated in the oil (live oil). We have not included any data from stirred autoclaves as there is no evidence to suggest that these generate similar turbulence fields or droplets to a jet. Indeed, the fact that the Paris et al. (2012) model, based on autoclave measurements, underestimates observed droplets by orders of magnitude (see green symbols in Figure D.1) supports the contention of Adams et al. (2013) that autoclaves generate a very different turbulence field (and hence droplet

TABLE D.2 Summary of Observations of Droplet Size Formed by a Subsurface Jet

Name	Facility	Press (m)	Flow (l/min)	Well Φ (mm)	Fluids	References
SINTEF 0	SINTEF Tower	5	0.2-5	0.5-3	Oil, air, Corexit	Brandvik et al., 2013
SINTEF 1	SINTEF Tower	5	1.2	1.5	Oil, Corexit	Brandvik et al., 2018
SINTEF 2	SINTEF Tower	5	1.2	1.5	Oil, dispersant	Brandvik et al., 2014
SINTEF 3	SwRI, Sintef T.	5-1,750	1.2	1.5	Oil, dispersant	Brandvik et al., 2019a
SINTEF 5	SwRI, Sintef T.	5-1,750	1.2	1.5	Live oil, gas, Corexit	Brandvik et al., 2019b
C-IMAGE	Hamburg autoclave	1,500	1-2	1.5	Oil, methane, n-dec.	Malone et al., 2018
SINTEF 6	OHMSETT	2	50-400	25-50	Oil, methane, Corexit	Brandvik et al., 2017
DeepSpill	Norwegian Sea	844	17	120	Diesel, LNG	Johansen et al., 2001

size) than jets. There are a number of other experimental observations of jets (e.g., Belore [2014], Masutani and Adams [2000], and Zhao et al. [2017b]), but these are unsuitable for various reasons.[3]

The lab experiments in Table D.2 (first six entries) span a wide range of conditions including discharge orifice scales of 1.5 to 50 mm and flow rates from 0.2 to 400 L/min. Most of the experiments come from Brandvik et al. (2014, 2017, 2018, 2019a,b) who have conducted roughly 200 individual experiments since 2011. Though none of the papers by Brandvik et al. provide error estimates on their measurements, they did numerous replicates that demonstrate the consistency of their observations. We did not use all of their experiments because there were so many replicates and we had to do all data entry manually. SINTEF 0 was not included because it has been used extensively by almost all of the models to calibrate them. It is also reassuring that the experiments of Malone et al. (2018) fit the same trend line as the similar experiments from Brandvik et al. (2013, 2014).

SINTEF 0, 1, 3, and 6 have been published in peer-reviewed journals and the remaining SINTEF work is documented in technical reports that have been available to the public for several years. The unpublished reports use similar methods, facilities, and instrumentation to SINTEF 0 and 1. Note that VDROP-J, Oildroplets, and the ASA models have used several of the experiments from SINTEF 0 in their model validation efforts, an implicit acceptance of the general methodologies employed by SINTEF.

SINTEF 0, 1, and 2 consisted of roughly 10-50 individual experiments each involving the release of an oil jet into sea water in the so-called SINTEF Tower Basin, a 6 m high by 3 m diameter cylinder. Droplet sizes were measured with a Laser In Situ Scattering and Transmissiometry (LISST) array located at 2 m above the discharge orifice. Some of the experiments had a second LISST located at 4m.

SINTEF 3 focused on the effects of pressure on the droplet size of dead oil and was the precursor for SINTEF 5, which considered pressure, gas and live oil. Most of the experiments were conducted in the large high-pressure chamber at Southwest Research Institute (SwRI), which consists of a 5.8 m long cylinder with a 2.3 m diameter capable of reaching pressures of 1,750 m of water. The Silhouette Camera (Davis et al., 2017, henceforth referred to as SilCam) was used and represented a major advance over a LISST-type device because (1) it was capable of simultaneously

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[3] Masutani and Adams had difficulty measuring the oil droplets because of limitations with their PDPA instrument. Zhao et al. were impacted by major fractionation due to their use of a horizontal jet. Belore studied a multiphase horizontal jet of gas and oil. Fractionation was an issue for them because of the inability of their primary measurement device (Laser In Situ Scattering and Transmissiometry) to differentiate between droplets and bubbles.

measuring both droplets and bubbles of any size above a few µm, and (2) it could measure much higher concentrations than the LISST.

The other small-scale set of observations comes from Malone et al. (2018) who conducted eight experiments in a pressurized column of 99 L. Flow rates and discharge orifice size were similar to SINTEF 0, 1, and 2.

An inherent weakness with these small-scale studies is their small discharge pipe and low flow rate, which were several orders of magnitude smaller than a DWH-like spill. The smaller scale means that models calibrated with this data are extrapolating several orders of magnitude to get to field scales.

To get to larger scales, SINTEF ran two sets of replicate experiments, one in the SINTEF Tower Basin used in the earlier studies and the other in the Ohmsett flow facility using a *vertical* discharge pipe. They looked at flow rates and discharge orifices that were at least an order of magnitude higher than in earlier studies. While Ohmsett is 200 m long by 20 m wide, it is only 2.4 m deep so it was necessary to apply a horizontal current (0.25-1.07 m/s), simulated by towing the discharge pipe, in order to dilute the oil sufficiently to take droplet measurements. For the Tower Basin, the layout was identical to SINTEF 0-2 except that two SilCams were used instead of the LISST, and the SilCams were placed at 5 m above the discharge to allow for sufficient dilution. The introduction of SilCams into the Tower Basin allowed for much higher flow rates and droplet sizes than explored in SINTEF 0, 1, and 2.

The overriding uncertainty for the Ohmsett experiments comes from the potential for significant droplet fractionation, which is the natural consequence of the fact that the oil plume gets pushed over to the side by the horizontal current. Zhao et al. (2017b) has shown how important fractionation can be with horizontal plumes. To counter the possible effects of fractionation, SINTEF 6 did extensive calculations (Brandvik et al., 2017) to determine where to position the SilCam to ensure that it was in the center of the oil plume.

Ultimately, the importance of fractionation in the Ohmsett experiments was not a concern. There were 12 experiments that were conducted in both the Tower Basin and the Ohmsett tank; the d_{50}s are compared in Figure D.2. The data points are color coded with red indicating questionable results (as determined by Brandvik et al., 2017) generally caused by oil clouding the limited volume of the Tower Basin. Even including these questionable data, the correlation coefficient squared is nearly 0.9. There is a slight bias with the Ohmsett d_{50} being 20%-30% larger than the Tower d_{50} at the larger d_{50}s. That said, that bias is coming from the questionable Tower results as denoted by the red symbols. The generally good comparison between the Ohmsett and Tower observations suggests that fractionation is of modest importance in the Ohmsett data at the larger droplet sizes. Hence, SINTEF 6 represents a valuable dataset for model calibration and validation, especially because its scales are more than an order of magnitude larger than the previous measurements.

The other large-scale dataset comes from the DeepStar field experiment, which consisted of four 1-hour field experiments in which gas and gas/oil mixtures were injected through a 12 cm nozzle at a depth of 840 m off the Norwegian Coast (Johansen et al., 2001, 2003). The most relevant of these is the second release involving a mixture of natural gas and marine diesel. Droplet volume distributions were reported on pages 63 and 64 of Johansen et al. (2001) for elevations of 4-5 m, 9-10 m, 14-22 m, and 34-55 m above the discharge (designated as Cases 5-8, respectively). There is considerable scatter in these cases but no obvious correlation to measurement height so we have simply averaged the d_{50} from all levels.

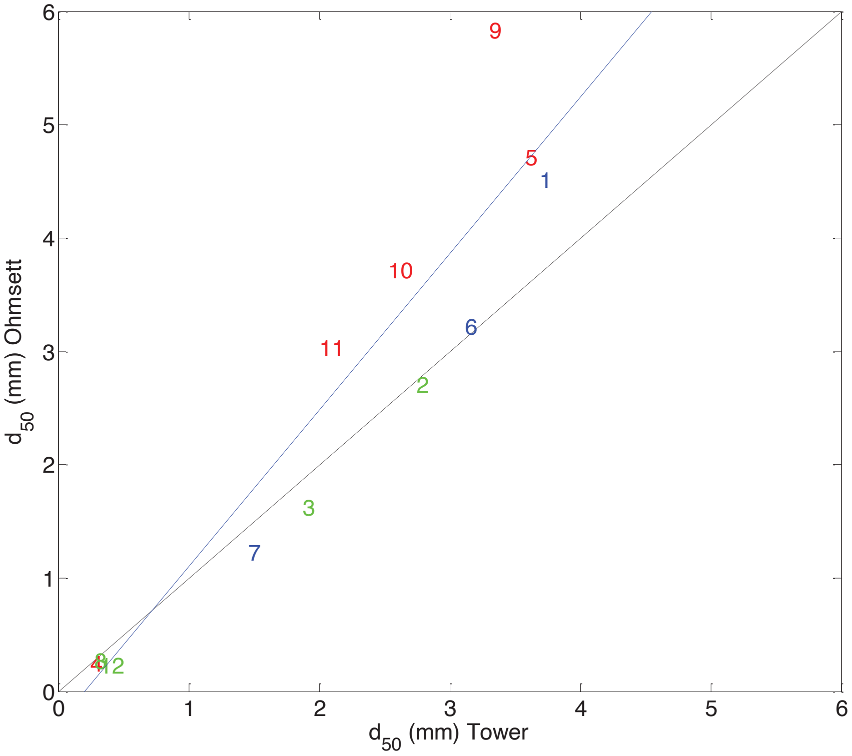

FIGURE D.2 Comparison of the d_{50} measured from replicate experiments in the Ohmsett and Tower facilities taken during SINTEF 6. Solid blue line is the least squares fit. Red numbers indicate questionable Tower data; blue numbers indicate "acceptable"; and green numbers indicate "excellent" as judged by Brandvik et al. (2017).

TABLE D.3 Summary of Experiments Used in Figure D.2

Exp. Name	Pipe Φ mm	Oil Flow L/min	Temp C°	IFT mN/m	GOR m^3/m^3	Oil ρ kg/m^3	Visc cp	DOR %	Source
\heartsuit	120	1,000	4	25.00	0.50	854	3.9	0.0	DeepSpill
\vartheta	1.5	1.2	13	13.40	0.00	832	7.1	0.0	SINTEF 2
\iota	1.5	1.2	13	2.30	0.00	832	7.1	1.0	SINTEF 2
\kappa	1.5	1.2	13	0.01	0.00	832	7.1	2.0	SINTEF 2
\lambda	1.5	1.2	75	13.40	0.00	832	2.8	0.0	SINTEF 2
\mu	1.5	1.2	75	6.80	0.00	832	2.8	1.0	SINTEF 2
\nu	1.5	1.2	75	0.10	0.00	832	2.8	2.0	SINTEF 2
\xi	1.5	1.2	50	12.20	0.00	832	4.1	0.0	SINTEF 2
\pi	1.5	1.2	50	13.10	0.00	832	4.1	1.0	SINTEF 2
\rho	1.5	1.2	50	0.02	0.00	832	4.1	2.0	SINTEF 2
\sigma	1.5	1.2	23	17.50	0.00	832	6.0	0.0	SINTEF 2
\varsigma	1.5	1.2	23	1.90	0.00	832	6.0	1.0	SINTEF 2
\tau	1.5	1.2	23	0.01	0.00	832	6.0	2.0	SINTEF 2
\phi	1.5	1.2	18	10.00	0.00	900	20.0	0.0	SINTEF 2
\psi	1.5	1.2	18	3.50	0.00	900	20.0	1.0	SINTEF 2
A	1.5	1.2	78	10.70	0.00	900	20.0	0.0	SINTEF 2
B	1.5	1.2	85	3.70	0.00	900	20.0	1.0	SINTEF 2
C	1.5	1.2	13	15.00	0.00	797	4.0	0.0	SINTEF 2
D	1.5	1.2	13	0.06	0.00	797	4.0	2.0	SINTEF 2
E	0.5	0.2	13	15.50	0.00	839	10.0	0.0	SINTEF 1
F	1.5	1.0	13	15.50	0.00	839	10.0	0.0	SINTEF 1
G	1.5	1.5	13	15.50	0.00	839	10.0	0.0	SINTEF 1
H	1.5	1.5	13	0.05	0.00	839	10.0	2.0	SINTEF 1
I	1.5	1.5	13	0.09	0.00	839	10.0	4.0	SINTEF 1
J	2.0	5.0	13	15.50	0.00	839	10.0	0.0	SINTEF 1
K	3.0	5.0	13	15.50	0.00	839	10.0	0.0	SINTEF 1
L	3.0	1.5	22	19.30	0.00	700	0.9	0.0	SINTEF 5
M	3.0	1.5	26	18.20	0.23	700	0.8	0.0	SINTEF 5
N	3.0	1.5	27	18.20	1.00	706	0.8	0.0	SINTEF 5
O	3.0	1.5	28	21.60	3.67	705	0.8	0.0	SINTEF 5
P	3.0	1.5	28	2.80	0.17	695	0.8	1.0	SINTEF 5
Q	3.0	1.5	32	3.27	0.67	695	0.7	1.0	SINTEF 5
R	3.0	1.5	36	3.87	2.33	690	0.7	1.0	SINTEF 5
S	3.0	1.5	27	3.87	0.00	700	0.8	1.0	SINTEF 5
T	3.0	1.5	27	18.60	0.00	776	0.8	0.0	SINTEF 5
U	3.0	1.5	37	21.00	0.43	774	0.7	0.0	SINTEF 5
V	3.0	1.5	36	21.50	1.13	773	0.7	0.0	SINTEF 5
W	3.0	1.5	49	19.50	4.00	773	0.6	0.0	SINTEF 5
X	3.0	1.5	50	1.77	3.93	772	0.5	1.0	SINTEF 5
Y	3.0	1.5	45	3.37	0.87	772	0.6	1.0	SINTEF 5
Z	3.0	1.5	41	3.37	0.40	773	0.6	1.0	SINTEF 5
a	3.0	1.5	40	3.57	0.00	773	0.6	1.0	SINTEF 5
b	3.0	1.5	22	22.00	0.00	764	0.8	0.0	SINTEF 5
c	3.0	1.5	30	20.00	0.93	773	0.7	0.0	SINTEF 5
d	3.0	1.5	31	21.30	0.00	775	0.7	0.0	SINTEF 5
e	3.0	1.5	34	20.00	0.80	755	0.6	0.0	SINTEF 5
f	3.0	1.5	38	2.87	1.00	753	0.6	1.0	SINTEF 5
g	3.0	1.5	39	2.87	0.00	754	0.5	1.0	SINTEF 5
h	3.0	1.5	35	3.27	0.00	752	0.6	1.0	SINTEF 5
i	3.0	1.5	37	0.57	0.87	770	0.6	1.0	SINTEF 5
j	25.0	50.0	13	20.00	0.00	826	4.6	0.0	SINTEF 6
k	25.0	80.0	13	20.00	0.00	826	4.6	0.0	SINTEF 6

continued

TABLE D.3 Continued

Exp. Name	Pipe Φ mm	Oil Flow L/min	Temp C°	IFT mN/m	GOR m^3/m^3	Oil ρ kg/m^3	Visc cp	DOR %	Source
l	25.0	80.0	4	20.00	0.00	826	5.1	0.0	SINTEF 6
m	25.0	50.0	5	20.00	0.00	826	5.0	0.0	SINTEF 6
n	25.0	80.0	5	20.00	0.00	826	5.0	0.0	SINTEF 6
o	25.0	120.0	6	20.00	0.00	826	5.0	0.0	SINTEF 6
p	25.0	120.0	6	20.00	0.00	826	4.9	0.0	SINTEF 6
q	25.0	50.0	5	0.20	0.00	826	5.0	1.0	SINTEF 6
r	25.0	80.0	5	0.20	0.00	826	5.0	1.0	SINTEF 6
s	25.0	120.0	6	0.20	0.00	826	5.0	1.0	SINTEF 6
t	32.0	300.0	6	20.00	0.00	826	4.9	0.0	SINTEF 6
u	32.0	120.0	13	20.00	0.00	826	4.6	0.0	SINTEF 6
v	32.0	80.0	13	20.00	0.00	826	4.6	0.0	SINTEF 6
w	32.0	300.0	5	0.20	0.00	826	5.0	1.0	SINTEF 6
x	32.0	120.0	7	0.20	0.00	826	4.9	1.0	SINTEF 6
y	32.0	120.0	7	0.02	0.00	826	4.9	2.0	SINTEF 6
z	32.0	120.0	3	0.20	0.00	826	20.0	1.0	SINTEF 6
1	50.0	200.0	13	20.00	0.00	826	4.6	0.0	SINTEF 6
2	50.0	300.0	13	20.00	0.00	826	4.6	0.0	SINTEF 6
3	50.0	300.0	7	20.00	0.00	826	4.9	0.0	SINTEF 6
4	50.0	400.0	7	20.00	0.00	826	4.9	0.0	SINTEF 6
5	50.0	300.0	15	0.20	0.00	826	4.2	1.0	SINTEF 6
\alpha	1.5	2.1	20	22.00	0.00	864	15.7	0.0	Malone 1.1
\beta	1.5	2.1	20	22.00	0.00	864	15.7	0.0	Malone 1.2
\gamma	1.5	2.0	20	32.00	0.00	817	1.3	0.0	Malone 2.1
\delta	1.5	2.1	20	32.00	0.00	817	1.30	0.0	Malone 2.2
\epsilon	1.5	1.1	20	55.00	0.00	741	1.10	0.0	Malone 3.1
\zeta	1.5	1.2	20	55.00	0.00	741	1.10	0.0	Malone 3.2
\eta	1.5	1.1	20	44.00	0.00	662	0.39	0.0	Malone 4.1
\theta	1.5	1.2	20	44.00	0.00	662	0.39	0.0	Malone 4.2

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APPENDIX E

CONSULTANTS' REPORT

Note from the committee**:** The work described in this appendix was commissioned by the committee with the purpose of better evaluating droplet size models—a key tool in modeling the oil fate in a subsea release. As discussed at length in Chapter 2, droplet models have been compared to varying degrees to laboratory experiments and one field study, but major questions remain as to how well these models scale to field conditions. Shortly after the committee began its work, Gros et al. (2017) published a dataset derived from the *Deepwater Horizon* measurements, which, after close review, the committee felt represented a reasonable benchmark for testing droplet models. Gros et al. (2017) only looked at two scenarios (0 and 0.4% dispersant-to-oil ratio [DOR]) of subsea dispersant injection using the VDROP-J model. The committee wanted to extend their original work by running the model with a DOR of 1%; a value which recent work suggests is much more optimal (Brandvik et al. 2014b). It also ran cases using droplet distributions by Spaulding et al. (2015, DWH NRDA) as well as a distribution predicted by the C-Image Consortium. Results from the consultants' report are discussed in Chapter 6.

Report on ***Deepwater Horizon*** Simulations with Different Droplet Size Distributions

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Introduction

We have completed simulations for the *Deepwater Horizon* blowout using different choices of subsea dispersant application rate and bubble and droplet size prediction models, as prescribed by the Committee on the Evaluation of the Use of Chemical Dispersants in Oil Spill Response. Each of these runs makes predictions for June 8, 2010, using our simulation package, the Texas A&M Oilspill Calculator (TAMOC) (Gros et al., 2017) and our 279 pseudo-component model of the *Deepwater Horizon* reservoir fluid (Gros et al., 2016). Model output includes dissolved concentrations in the deepwater intrusion layer, mass flow rate of compounds to the air/water interface, and water column concentrations between the intrusion layer and sea surface. All model parameters except for bubble and droplet size and interfacial tension matched those used in our paper (Gros et al., 2017), published in the *Proceedings of the National Academy of Sciences of the United States of America* (*PNAS*).

Table E.1 presents a description of each case simulated in this study. We report here the model results for all cases in Table E.1; Case 3 was not defined and has been deleted. Each case in the table represents a different approach for predicting the droplet size distribution and/or a different assumed DOR. For some methods (Cases 1 and 5), only the median droplet size d_{50} is provided by

TABLE E.1 Description of the Cases and Size Distributions Used in the Simulations

Case	d_{50} [mm]	[—]	DOR [%]	d_{max} Rule	Micro Droplets [%]	Description and Source
1	10	0.5	0	$d = d_{max}$ if the predicted distribution has $d > d_{max}$	0.2	Untreated upper limit of droplet size distribution
2	vdrop-j	vdrop-j	0	N/A	0.5	Untreated case already simulated and reported in Gros et al. (2017)
4	vdrop-j	vdrop-j	0.4	N/A	1.1	Treated case (hindcast value) already simulated and reported in Gros et al. (2017)
5	0.17; 3.3	0.5	30% treated; 70% untreated	N/A	–16.7	Bimodal distribution assumed using partial dispersant mixing
6	c-image	N/A	0	N/A	–1.7	Untreated case provided by C-IMAGE. Number size distributions were provided, which we converted to volume size distributions
7	vdrop-j	vdrop-j	1.0	N/A	–25.2	Treated case with optimal DOR

the method. In these cases, the size distribution is estimated from a log-normal distribution of log standard deviation σ_N provided in the table. For Case 1, this approach predicts droplet sizes larger than the maximum stable droplet size. For this case, we truncate the distribution in order to retain the desired d_{50}.

This report is organized as follows. Sections 1 to 6 report the results of each simulation case using the data comparison and analysis formats already reported in Gros et al. (2017). These sections compare measured and predicted fractionation indices for several compounds in the deepwater intrusion layer and at the sea surface. These sections also report the petroleum fluids mass balance among the deepwater intrusion, mid-ocean water column, and the sea surface. Throughout this report, we consider the term *petroleum fluids* to mean the whole reservoir fluid, including the C1-C5 compounds. Section 7 explains our method to compute dissolved concentrations between the intrusion layer and the sea surface, where individual Lagrangian bubbles and droplets transit the water column. This section also shows sample results for benzene. We conclude this report with a short discussion in Section 8.

1. Case 1: Untreated Upper-Limit of Droplet Size Distribution

Figure E.1 shows the gas bubble sizes (top panel) and oil droplet sizes (lower panel) used in the simulations for Case 1, designed as the untreated upper-limit of the droplet size distribution. The gas bubble sizes were computed using the empirical equations in Wang et al. (2018) with the gas properties computed by our model without dispersant addition. The oil droplet sizes have a d_{50} = 10 mm, and the distribution is truncated at the maximum stable droplet size (Clift et al., 1978). The oil droplet size distribution was truncated because any other redistribution of oil mass would

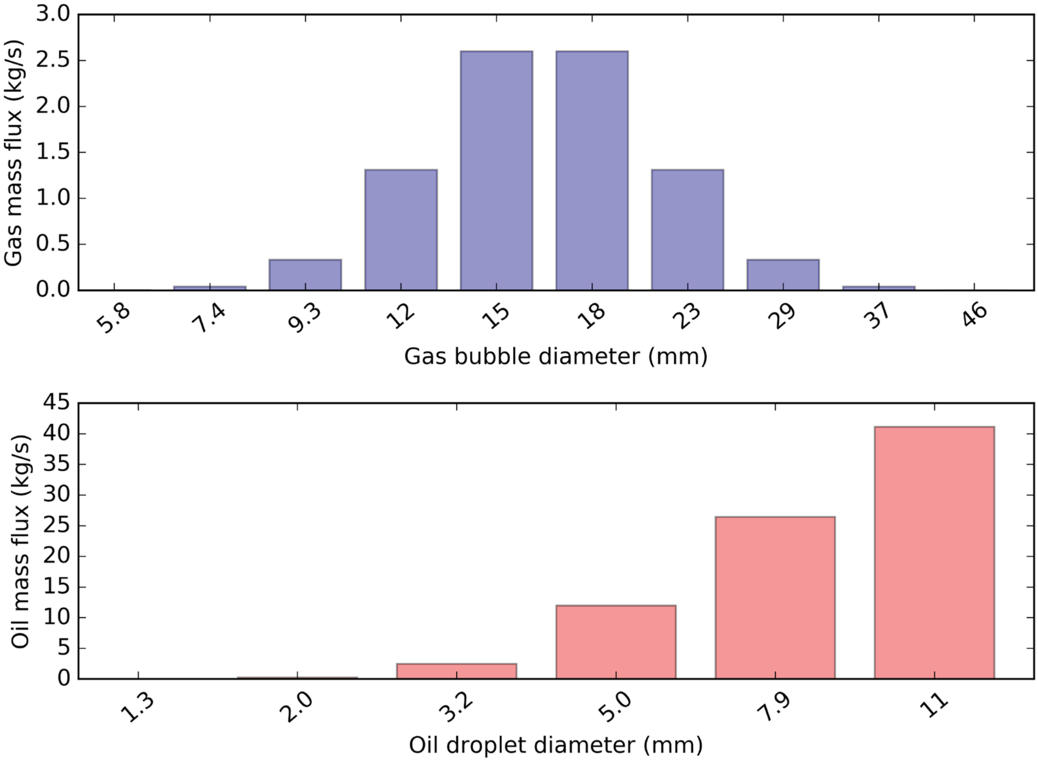

FIGURE E.1 Initial bubble and droplet size distribution for Case 1.

change the prescribed d_{50}-value of the distribution. Because the maximum stable bubble size is quite large, the bubble size distribution did not have to be truncated.

We show the model predictions compared to measured field data in Figure E.2, using the same figure format as model-data comparisons in Figure 3 of our *PNAS* paper (Gros et al., 2017). This figure and all similar figures to follow are organized as follows. Panels A and B report the model predictions for the combined dissolved and liquid petroleum and compare the model values to measured data from Conductivity, Temperature, and Depth casts within 10 km of the wellhead. See the Supporting Information for Gros et al. (2017) for the details of the sources and time periods of the field data used here for comparison; we considered all data available within the 10 km radius of the wellhead and representative of conditions on June 8, 2010. Panel A reports the fractionation index relative to methane for three constituents of the released petroleum in the subsurface intrusion layer (900 m to 1,300 m water depth). Panel B reports fractionation indices relative to benzene in the intrusion layer for several additional selected components of the simulated oil. In Panel B, the blue bars represent the raw model output and the orange bars represent the model output with a fixed, constant fraction of microdroplets added to the intrusion layer. The fraction of microdroplets is adjusted for each case separately to achieve the best possible agreement between the model and the measurements for the 16 sparingly-soluble compounds from phenanthrene to pristane. This fraction of microdroplets is reported for each case in Table E.1. In Panel C, we report results for the fraction of spilled petroleum arriving at the sea surface in comparison to measurements by Ryerson et al. (2012).

The results for Case 1 show that less of the released oil entered the intrusion as dissolved or liquid petroleum than was observed (under-prediction of model results in Panels A and B). Instead, more volatile organic compounds are predicted to reach the sea surface than observed (over-predictions of model results in Panel C). These results are also summarized in Figure E.3, which reports the model prediction of the petroleum mass budget throughout the water column for Case 1 without the addition of the fitted microdroplets (e.g., similar to the blue bars in Figure E.2). The large oil droplets of this case dissolve slowly (low surface area to volume ratio), rise quickly (have a short time to dissolve), and bring more of the light components to the sea surface than were observed by the atmospheric measurements. Hence, this droplet size over-predicts the best-fit droplet size for our model for June 8, 2010.

2. Case 2: Untreated Sensitivity Simulation

Figure E.4 shows the gas bubble sizes (top panel) and oil droplet sizes (lower panel) used in the Case 2 simulations. These sizes were predicted from the VDROP-J model using the gas and oil properties we predict if no dispersants were used. This case was already simulated and reported in our paper (Gros et al., 2017). Because dispersants were injected on this day, this case represents a hypothetical sensitivity study with respect to dispersant effectiveness.

We show the model predictions compared to measured field data in Figure E.5, using the same figure format as in Figure E.2. In this case, the simulation under-predicts the fraction of released petroleum entering the intrusion layer. By adding microdroplets, the simulation results can match observations for insoluble components of the oil, but the lighter compounds remain under-predicted in the intrusion layer, suggesting less dissolution is occurring in the model than was observed. This is consistent with an over-predicted droplet size, and is corroborated by the predictions at the sea surface, which show more oil reaching the surface in the model than the observations. The petroleum mass budget predicted by our model for this case is shown in Figure E.6 without the addition of the fitted microdroplets. Like Case 1, this droplet size over-predicts the best-fit droplet size for our model for June 8, 2010.

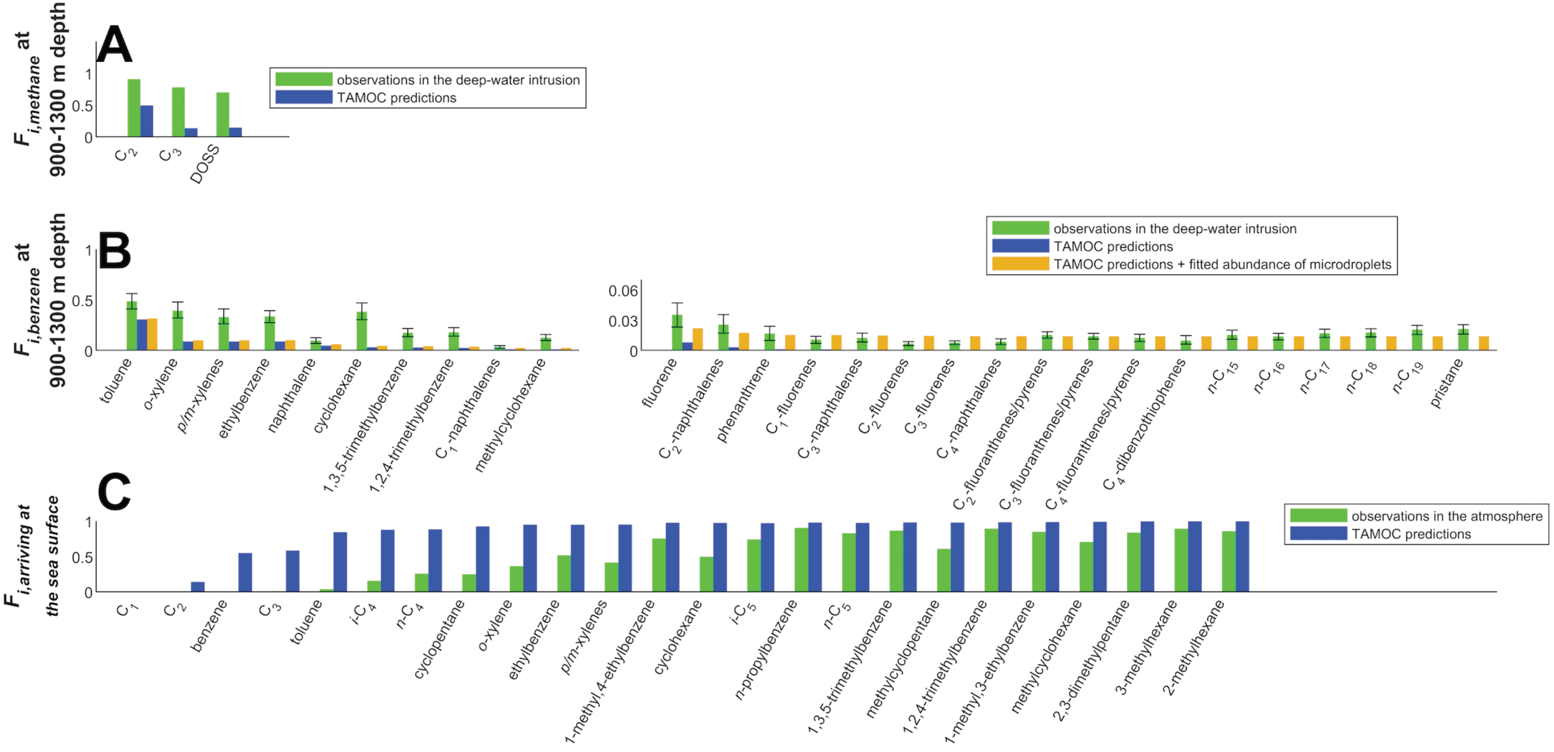

FIGURE E.2 Simulation results for Case 1.

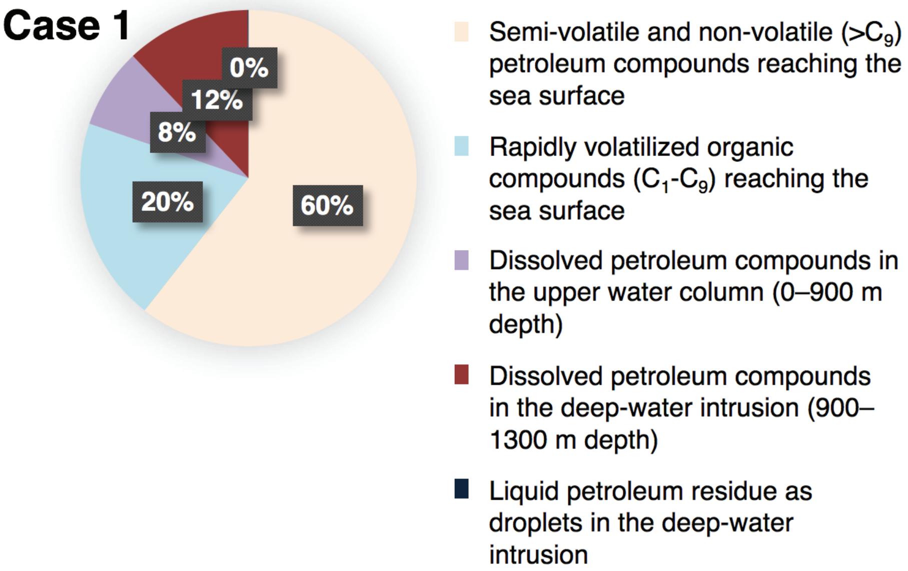

FIGURE E.3 Simulated fate and transport of petroleum fluids for Case 1 without calibrated microdroplets.

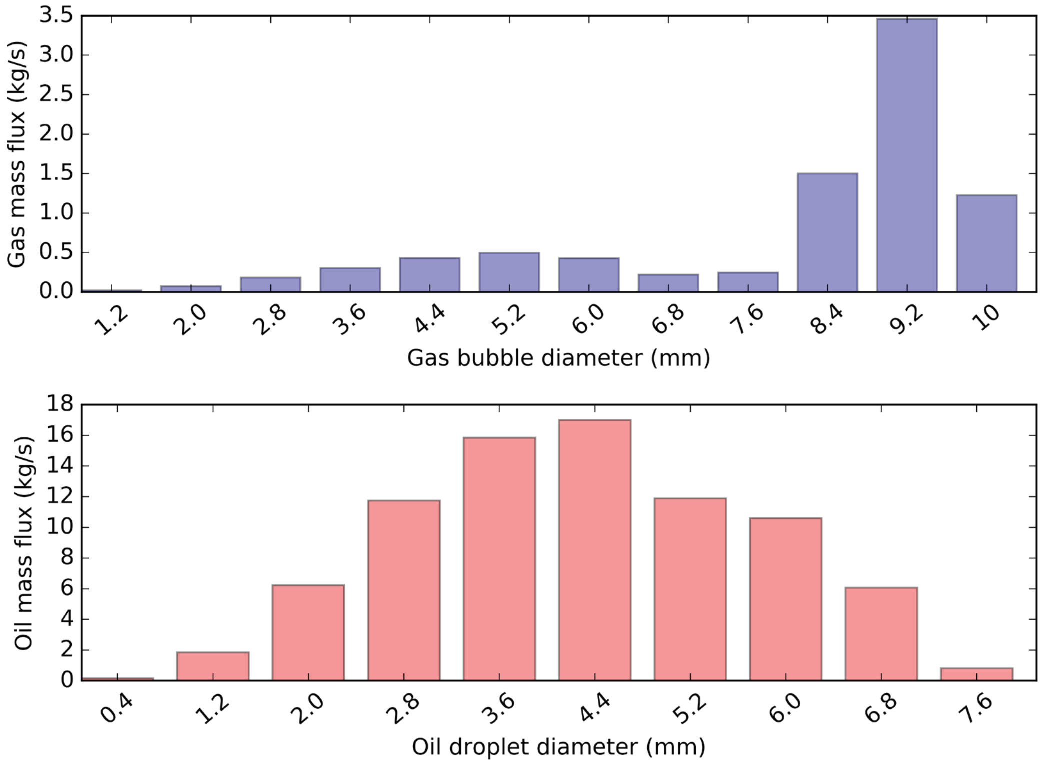

FIGURE E.4 Initial bubble and droplet size distribution for Case 2.

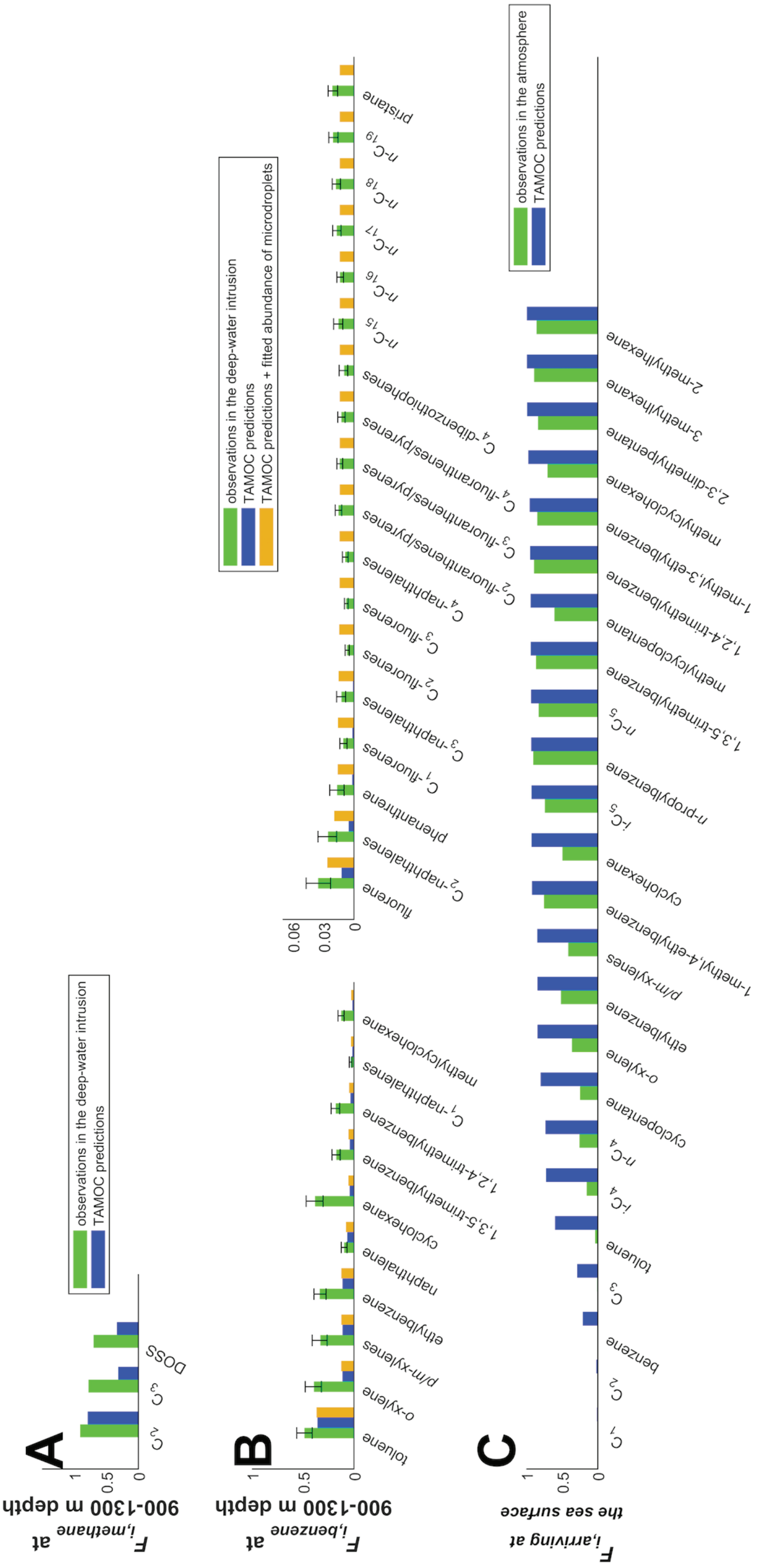

FIGURE E.5 Simulation results for Case 2.

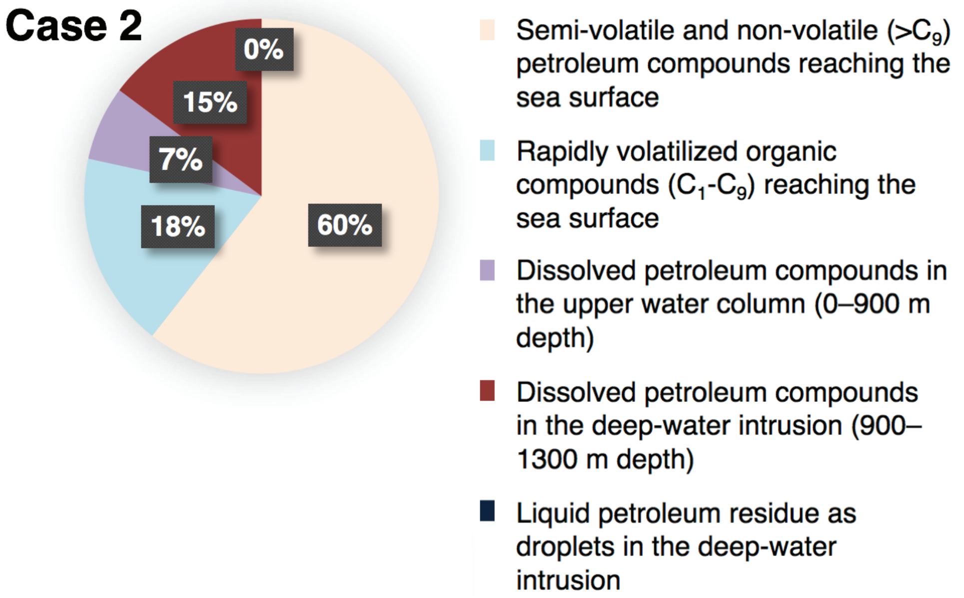

FIGURE E.6 Simulated fate and transport of petroleum fluids for Case 2 without calibrated microdroplets.

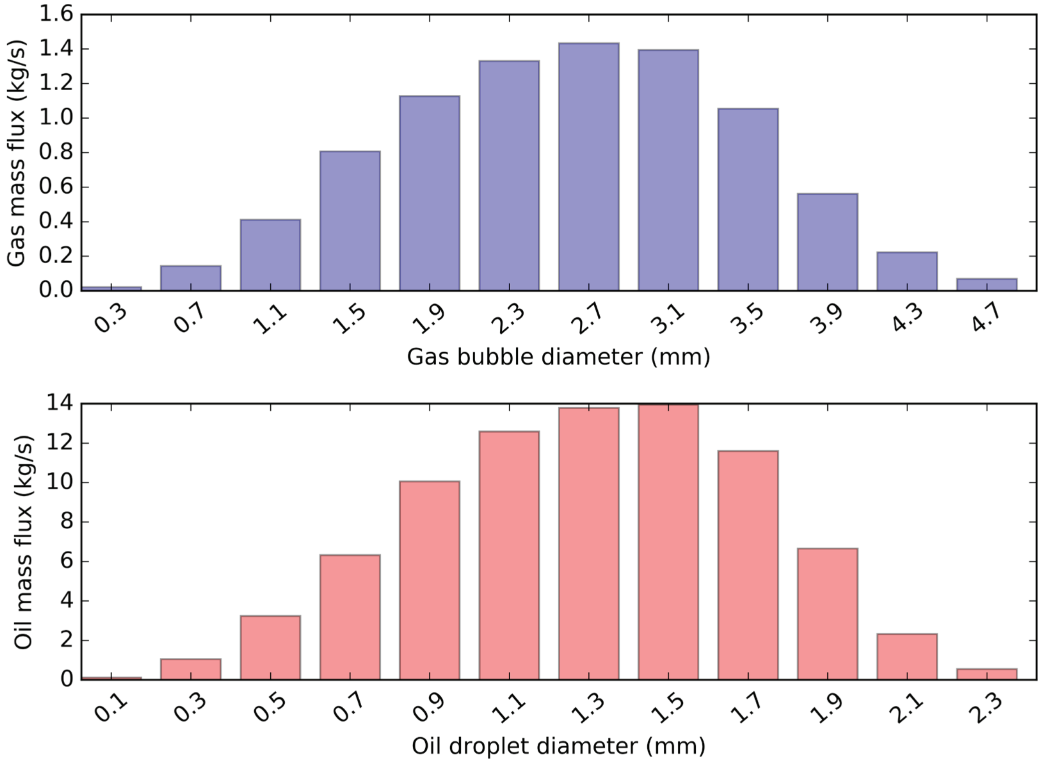

FIGURE E.7 Initial bubble and droplet size distribution for Case 4.

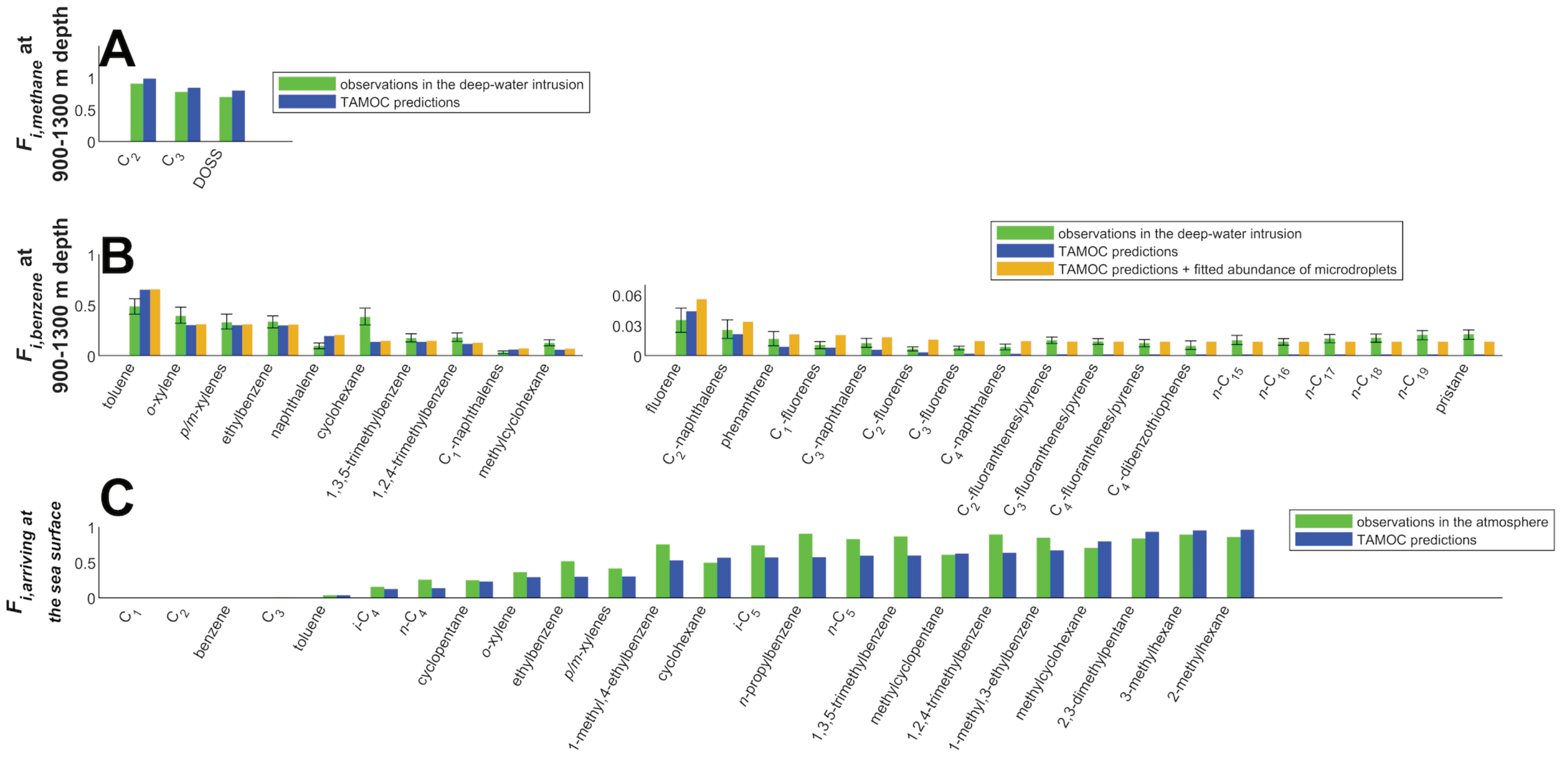

FIGURE E.8 Simulation results for Case 4.

3. Case 4: Best-Case Hindcast Simulation

Figure E.7 shows the gas bubble sizes (top panel) and oil droplet sizes (lower panel) used in the Case 4 simulations. These sizes were predicted from the VDROP-J model using the gas and oil properties we predict for a DOR of 0.4%, our estimate of the actual DOR during this day assuming full mixing of dispersant with the quantity of oil exiting the broken Macondo wellhead. This case was already simulated and reported in our paper (Gros et al., 2017). Because dispersants were injected on this day, this case represents our best-case hindcast of the behavior of the *Deepwater Horizon* oil spill on this day using our model.

We show the model predictions compared to measured field data in Figure E.8, using the same figure format as in Figure E.2. In the intrusion layer (Panels A and B) the model predicts the fractionation of light, soluble compounds well, with some constituents over-predicted (e.g., toluene, naphthalene) and others under-predicted (o-xylene, cyclohexane). With a small quantity of fitted microdroplets (1.1%, see Table E.1), the results for insoluble compounds are close to the observations, and the predictions for soluble compounds are mostly unchanged. At the sea surface (Panel C), model predictions for the fraction of oil reaching the surface corresponds well with the observations, with most compounds slightly under-predicted by the model. The petroleum mass budget predicted by our model for this case is shown in Figure E.9 without the addition of the fitted microdroplets. Because these results were obtained using a DOR representative of June 8, 2010, and the model results largely show good agreement with the observations, this droplet size corresponds to the best-fit droplet size for our model for this day.

4. Case 5: Partial Mixing of Dispersant

Figure E.10 shows the gas bubble sizes (top panel) and oil droplet sizes (lower panel) used in the Case 5 simulations. These sizes were predicted using a procedure similar to that used by RPS ASA used for June 8, 2010, in the NRDA documents and that was also reported in Li et al.

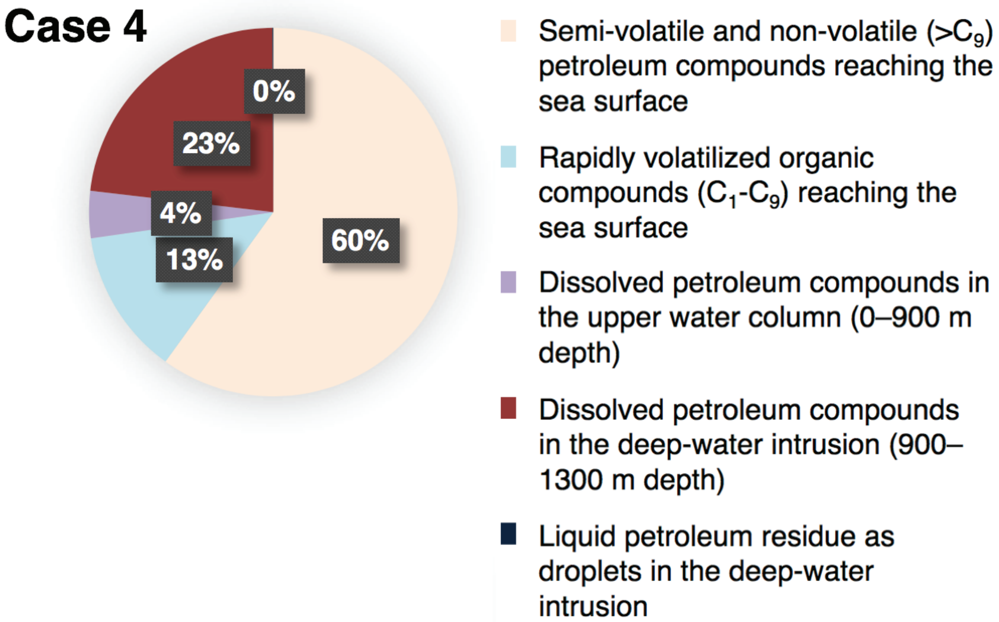

FIGURE E.9 Simulated fate and transport of petroleum fluids for Case 4 without calibrated microdroplets.

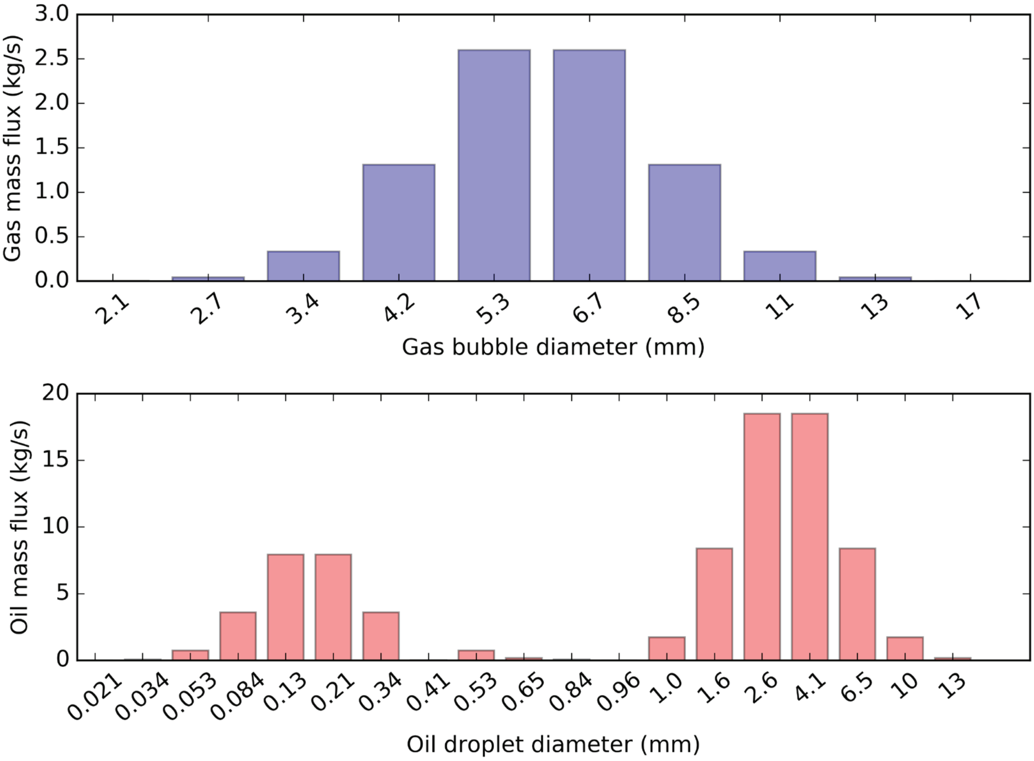

FIGURE E.10 Initial bubble and droplet size distribution for Case 5.

(2016). Following this method, dispersant is assumed to only treat some of the oil, and for Case 5, we assumed that the dispersant treatment fraction was 30%. The size distribution is taken as the sum of the distributions for the treated fraction (with d_{50} of 0.17 mm, see Table E.1) and untreated fraction (with d_{50} of 3.3 mm, Table E.1). Each size distribution was assumed log-normal with a log standard deviation = 0.5. Gas bubble sizes are computed using the formula in Wang et al. (2018) with an interfacial tension reduction factor of 5.4 times.

We show the model predictions compared to measured field data in Figure E.11, using the same figure format as in Figure E.2. In this case, the simulation significantly over-predicts the fraction of released petroleum entering the intrusion layer, especially for the insoluble compounds. The slanted black lines for the fluorene predictions indicate that the actual model value plots above the present *y*-axis. By removing microdroplets (–16.7%, see Table E.1), the simulation results can match observations for insoluble components of the oil, but the lighter compounds remain over-predicted in the intrusion layer, suggesting more dissolved petroleum is entering the intrusion in the model than was observed. The results at the sea surface (Panel C) also show a slight over-prediction relative to the measured data of the mass flow rate to the surface of the lighter compounds, indicating somewhat less dissolution overall occurring in the model throughout the water column than observed. The petroleum mass budget predicted by our model for this case is shown in Figure E.12 without the addition of the fitted microdroplets.

We can draw several conclusions from these results. Because the model predictions in the intrusion layer over-predict the observations, the modeled fraction of small droplets was over-predicted. When we subtract microdroplets, the predictions for soluble compounds remain over-predicted;

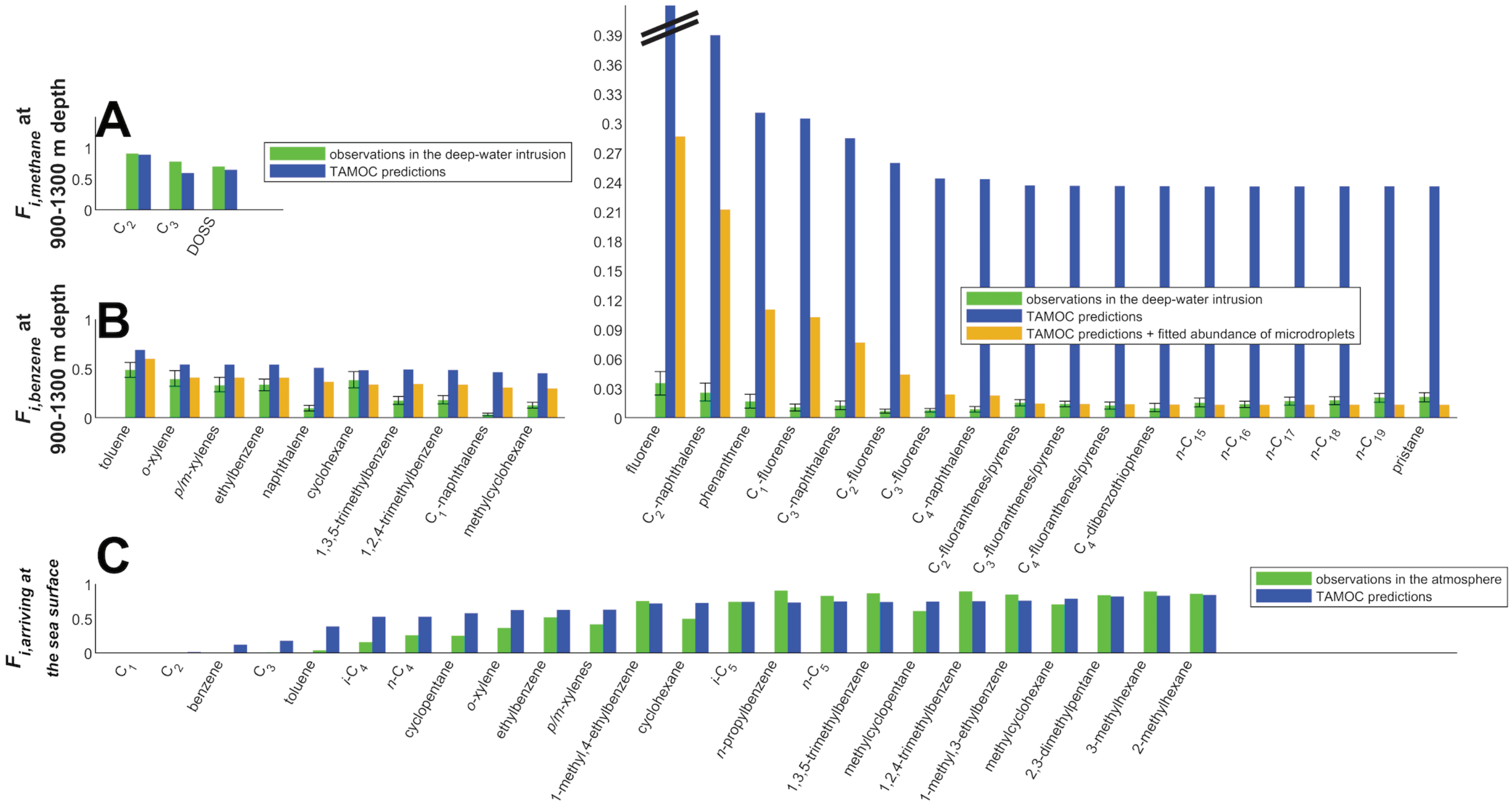

FIGURE E.11 Simulation results for Case 5.

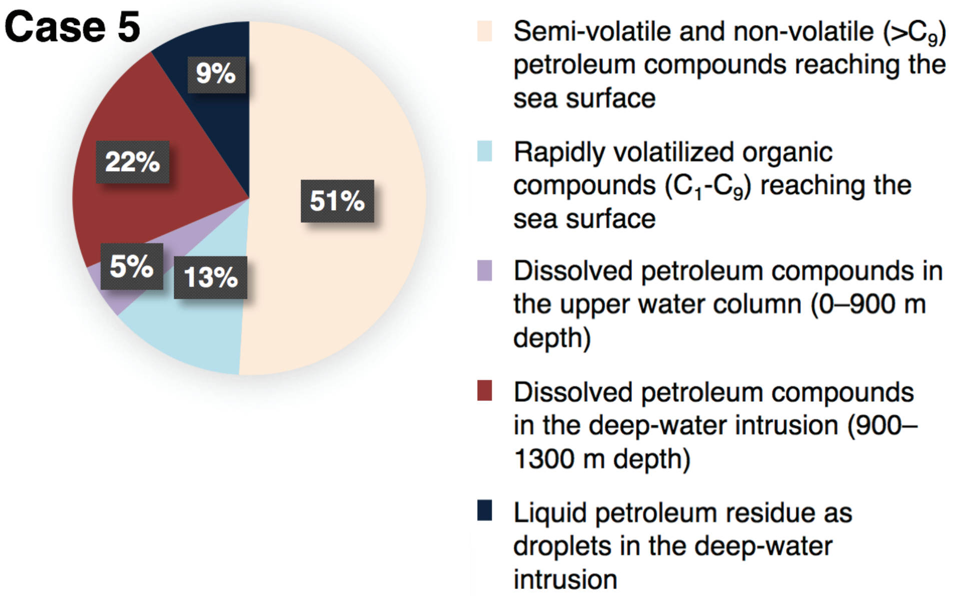

FIGURE E.12 Simulated fate and transport of petroleum fluids for Case 5 without calibrated microdroplets.

hence, the mass fraction of oil in the small droplets was over-predicted, yielding more dissolution than observed. On the other hand, the model predicts too much of several volatile organic compounds (VOCs) reaching the surface, which is consistent with over-predicting the mass fraction of large droplets for the untreated fraction of the distribution. Together, these results suggest to us that the hypothesis of incomplete dispersant mixing is not supported by these simulations: there are too many small droplets and large droplets for this type of distribution to produce results that fit the observations using our model. We conclude instead that all of the oil was treated somewhat (which would give a smaller maximum droplet size and less VOCs reaching the surface), and this more dilute treatment reduced the dispersant effectiveness (which would give a larger minimum droplet size and less dissolved compounds sequestered in the intrusion layer). Such a situation agrees with the observed fractionation indices and is close to the case of complete dispersant mixing across the plume (e.g., Case 4, above).

5. Case 6: Untreated Size Distributions Prescribed by C-IMAGE

Figure E.13 shows the gas bubble sizes (top panel) and oil droplet sizes (lower panel) used in the Case 6 simulations. These sizes were predicted by researchers in the C-IMAGE consortium and provided to us by Steve Murawski as number size distributions. We converted these number distributions to equivalent volume size distributions, and these latter volume size distributions are shown in the figure herein. Because dispersants were injected on June 8, 2010, this untreated case represents a hypothetical sensitivity study with respect to the true hindcast, which would include the effect of dispersant injection.

We show the model predictions compared to measured field data in Figure E.14, using the same figure format as in Figure E.2. In this case, the simulation strongly over-predicts the fraction of released petroleum entering the intrusion layer. By removing microdroplets (–1.7%, see Table E.1), the simulation results can match observations for the most insoluble components of the

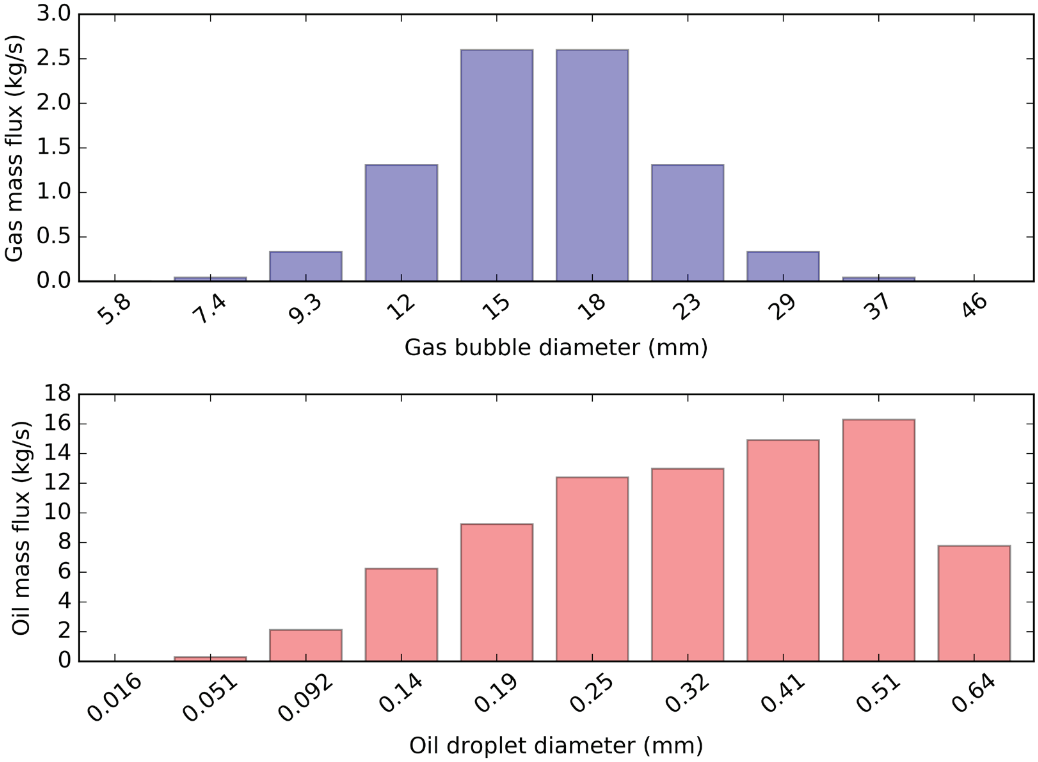

FIGURE E.13 Initial bubble and droplet size distribution for Case 6.

oil (right half of Panel B), but the lighter compounds remain over-predicted in the intrusion layer, suggesting more dissolution is occurring in the model than was observed. This is consistent with an under-predicted droplet size, and is corroborated by the predictions at the sea surface, which show much less oil reaching the surface in the model than the observations. The petroleum mass budget predicted by our model for this case is shown in Figure E.15 without the addition of the fitted microdroplets. Based on these data, this droplet size under-predicts the best-fit droplet size for our model for June 8, 2010.

6. Case 7: Hypothetical Optimal Dispersant Treatment Scenario

Figure E.16 shows the gas bubble sizes (top panel) and oil droplet sizes (lower panel) used in the Case 7 simulations. These sizes were predicted from the VDROP-J model using the gas and oil properties we predict for a DOR of 1.0% and assuming full mixing of dispersant with the quantity of oil exiting the broken Macondo wellhead. VDROP-J predicts droplet sizes in bins of 100 μm most of the bubble and droplet sizes were small for this case, which is why so few bins were used in the simulations. This DOR is higher than actually occurred on June 8, 2010, and represents an optimal DOR to achieve greater dispersant effectiveness at a low DOR. Hence, this case represents a hypothetical estimate of what might have resulted were a higher DOR used at the *Deepwater Horizon* oil spill on this day.

We show the model predictions compared to measured field data in Figure E.17, using the same figure format as in Figure E.2. In this case, the simulation strongly over-predicts the frac-

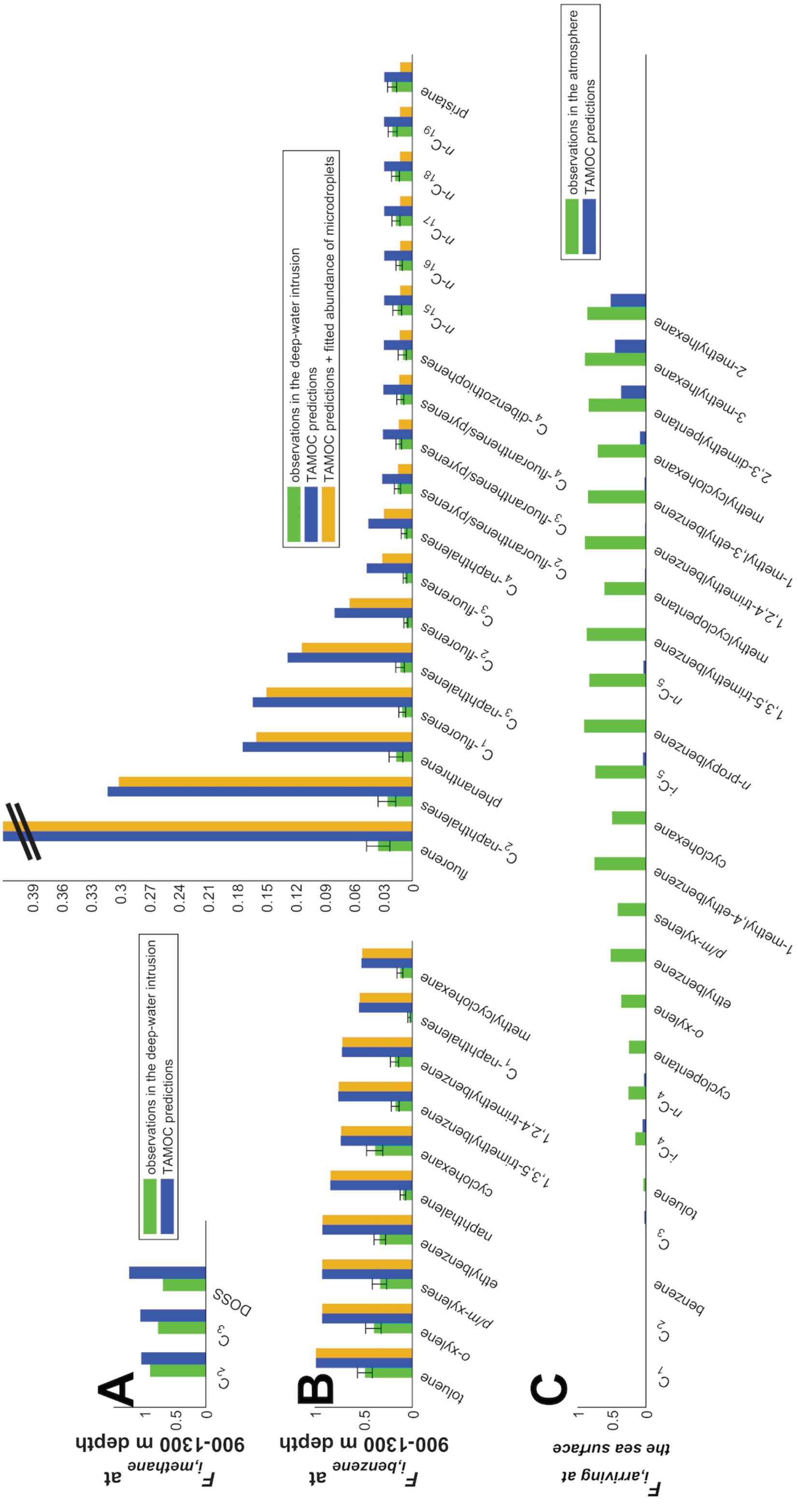

FIGURE E.14 Simulation results for Case 6.

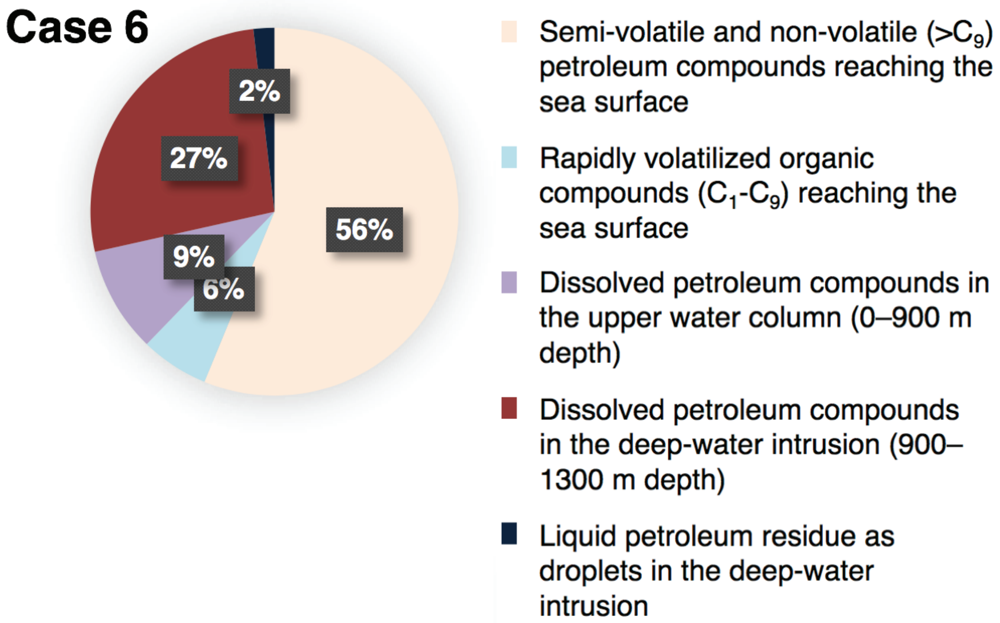

FIGURE E.15 Simulated fate and transport of petroleum fluids for Case 6 without calibrated microdroplets.

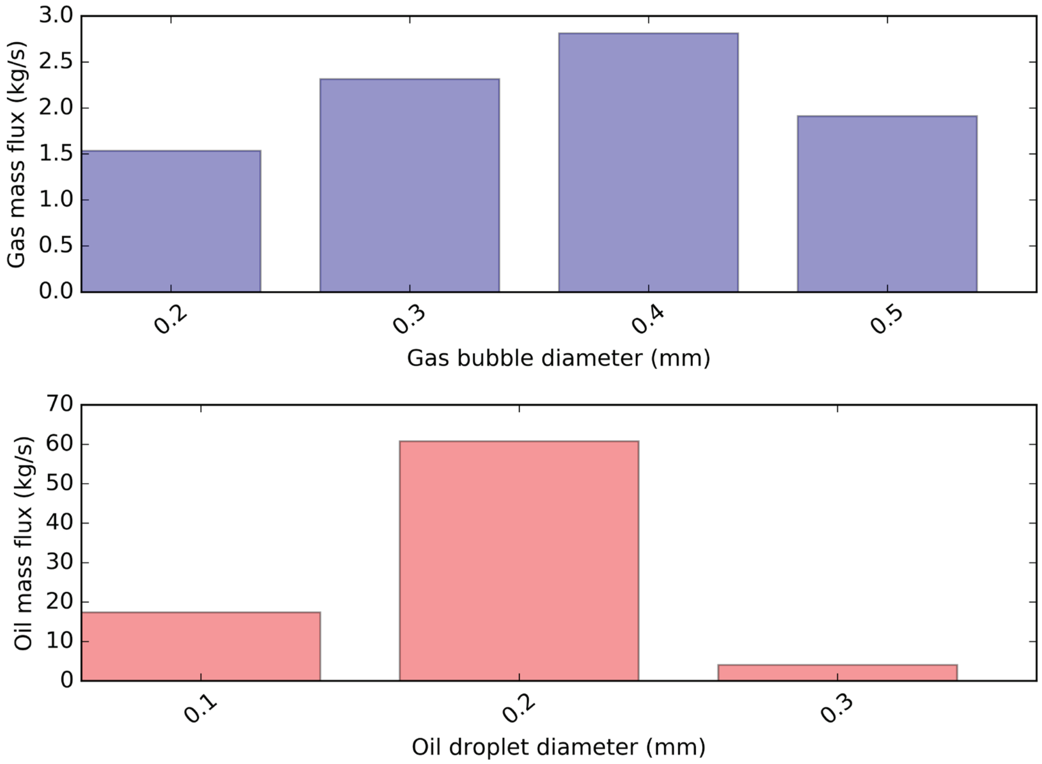

FIGURE E.16 Initial bubble and droplet size distribution for Case 7.

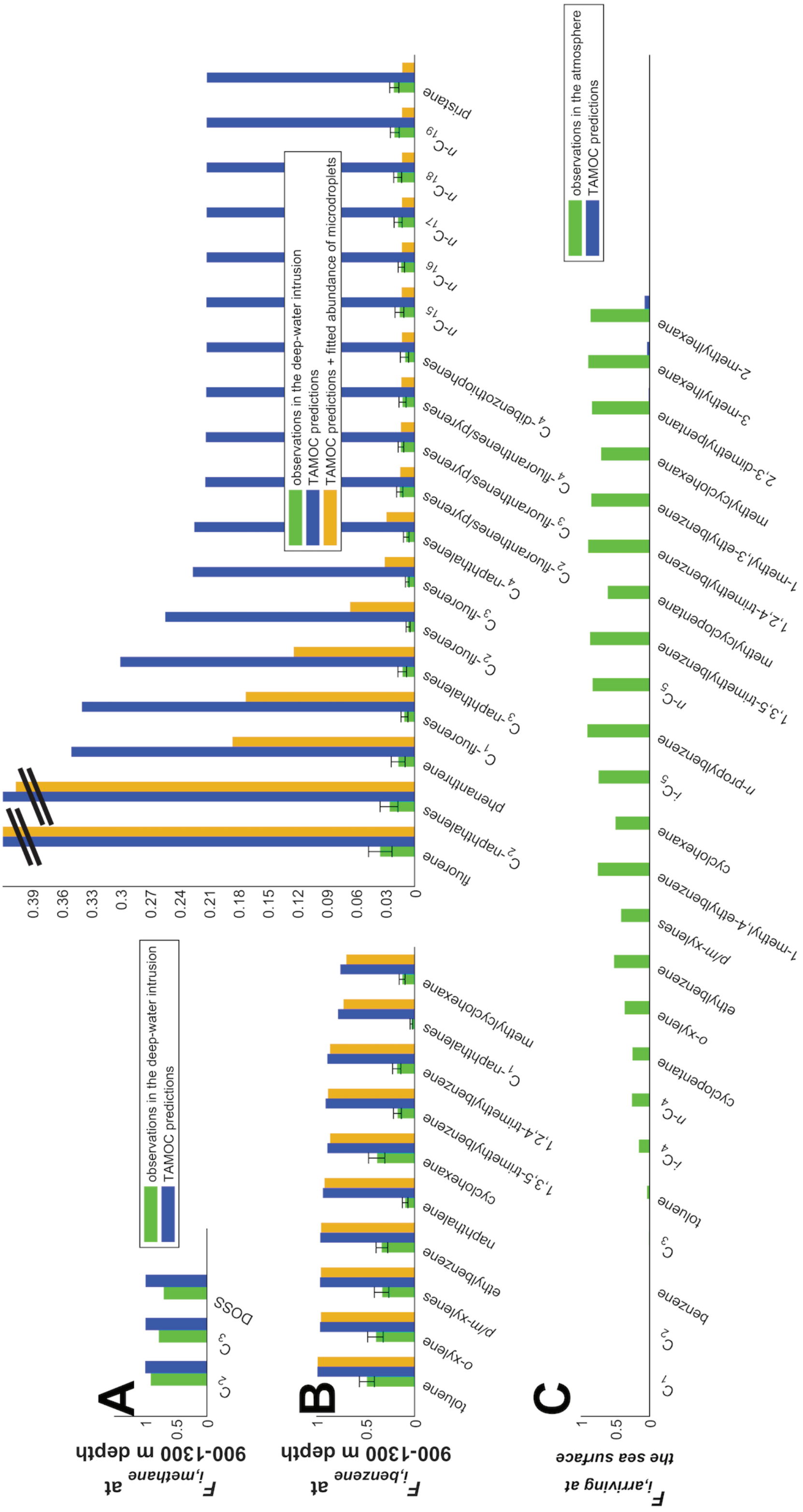

FIGURE E.17 Simulation results for Case 7.

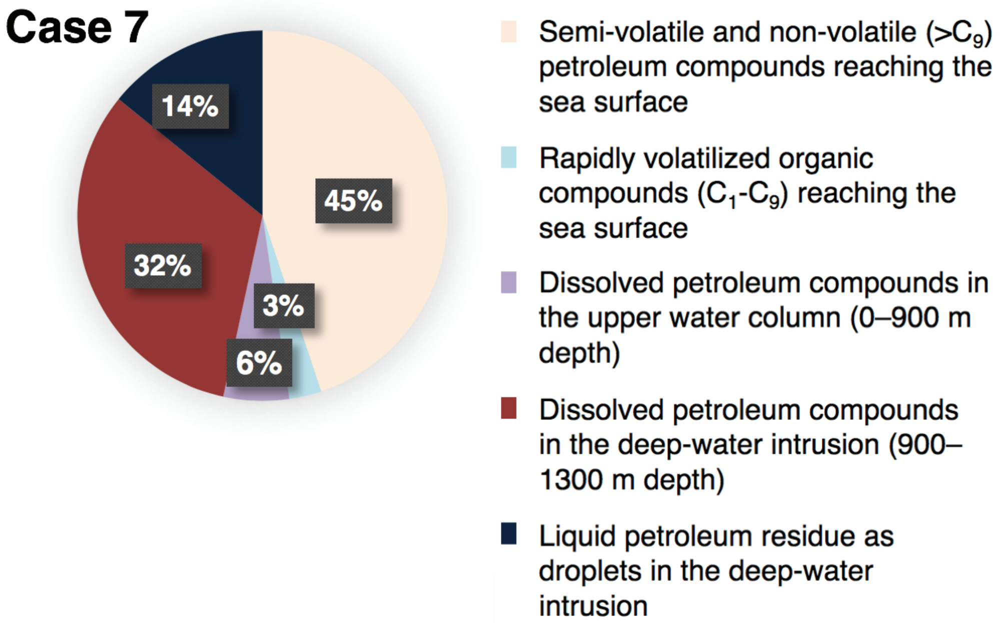

FIGURE E.18 Simulated fate and transport of petroleum fluids for Case 7 without calibrated microdroplets.

tion of released petroleum entering the intrusion layer. By removing microdroplets (–25.2%, see Table E.1), the simulation results can match observations for the most insoluble components of the oil (right half of Panel B). This suggests that up to 25% more of the released insoluble compounds could have been funneled to the deep intrusion if this higher DOR were used. Additionally, these small droplets dissolve faster, and the predictions with and without microdroplets over-predict the fraction of soluble petroleum entering the intrusion, also increasing the total amount of petroleum sequestered in the deep ocean. This is consistent with the predictions at the sea surface, which show almost none of the compounds of the oil plotted in Panel C reaching the surface in the model. The petroleum mass budget predicted by our model for this case is shown in Figure E.18 without the addition of the fitted microdroplets. Hence, this droplet size distribution causes a significantly greater fraction of the released petroleum to be sequestered in the ocean than occurred at the actual DOR of 0.4% (Case 4, above).

7. Concentration in the Water Column Above the Main Intrusion

The simulations for each of the cases reported above tracked the concentrations of dissolved hydrocarbons and the masses of gas and liquid petroleum in the initial nearfield plume and the deepwater intrusion layer and the masses of gas and liquid petroleum in the water column between the intrusion layer and the sea surface. For injury assessment, the concentrations of dissolved hydrocarbons throughout the ocean water column are needed. These are not immediately available because oil droplets and gas bubbles rise as individual Lagrangian particles between the deep intrusion layer and the surface, and there is no associated control volume of seawater to use to track the dissolved concentrations. To predict these concentrations, we developed a new model for the dissolved phase concentration associated with a stream of Lagrangian particles.

Our new model for dissolved-phase concentration in the mid-ocean water column is based on a solution to the advection diffusion equation in seawater with the source term of dissolved mass coming from the on-going dissolution of the Lagrangian particles. TAMOC predicts the steady-state dissolution for each Lagrangian particle by the mass balance equation

$$\frac{d\dot{m}_i}{dz} = \dot{m}_i^{'} = -\frac{A\beta_i \dot{n}}{u_s}\left(C_{s,i} - C_{a,i}\right) \tag{1}$$

where $\dot{m}_i^{'}$ is the steady-state mass flow rate per unit length of chemical component *i* in Lagrangian particles of a given size, *A* is the surface area of the particles, *β* is the mass transfer coefficient for chemical component *i*, $\dot{n}$ is the number flux of bubbles in the present particle class, *β* is the slip velocity of the particles, $C_{s,i}$ is the solubility of component *i* at the bubble-water interface, and $C_{a,i}$ is the concentration of component *i* in the ambient water, far away from the bubble, taken as zero for petroleum compounds.

If we use this mass flow rate $\dot{m}_i^{'}$ as the source term in the advection diffusion equation, an analytical solution exists if we assume that $\dot{m}_i^{'}$ is constant with height (an assumption that is approximately valid locally at each water depth) and that the horizontal transport is in the advection-dominant regime. The analytical solution in this case for a uniform crossflow of velocity *U* is

$$C\left(x,y\right) = \frac{\dot{m}_i^{'}}{\sqrt{4\pi xUE}} \exp\left(-\frac{Uy^2}{4Ex}\right) \tag{2}$$

where *E* is the turbulent eddy diffusivity, *x* is taken parallel with *U*, and the source is injected at the coordinate (0,0). The model in Equation (2) is valid in the advection-dominated regime, at a location *x*, a distance larger than *L* downstream of the bubble stream, where

$$L = \frac{E}{\alpha U} \tag{3}$$

and *α* is a parameter, greater than 10. Our observations of turbulent diffusivity in the deep Gulf of Mexico give values of $E_t = 5 \times 10^{-4}$ m^2/s (Wang et al., 2016); hence, *L* is a very short distance downstream at typical ocean currents in the Gulf of Mexico of between 2 and 30 cm/s.

We compute these concentrations for each chemical component in the gas bubbles and oil droplets above the intrusion layer using our full 279 pseudo-component model of the *Deepwater Horizon* reservoir fluid. We compute all concentrations at a distance 10 km downstream of the broken Macondo wellhead, and the total concentration of a given chemical component is the superposition of the contributions from each bubble and droplet size in each simulation. Equation (2) is valid if the particles in a stream of bubbles or droplets do not spread out. However, in reality, the particles are already distributed across the plume width σ_0 before exiting the intrusion layer and continue to spread by horizontal turbulent diffusion between the intrusion layer and a height *z* where Equation (2) is evaluated. We account for this spreading by computing Equation (2) for 1,000 particles Gaussian-distributed over the predicted cloud width, given by

$$\sigma = \sqrt{\sigma_0^2 + 2E_t t} \tag{4}$$

where *t* is the travel time for a given particle from the intrusion layer to *z*. Because most of the spreading occurs in the plume (i.e., $\sigma \approx \sigma_0$), our results are weakly dependent on the value of E_t. The total concentration is the superposition of the contributions for each of the 1,000 simulated bubbles or droplets.

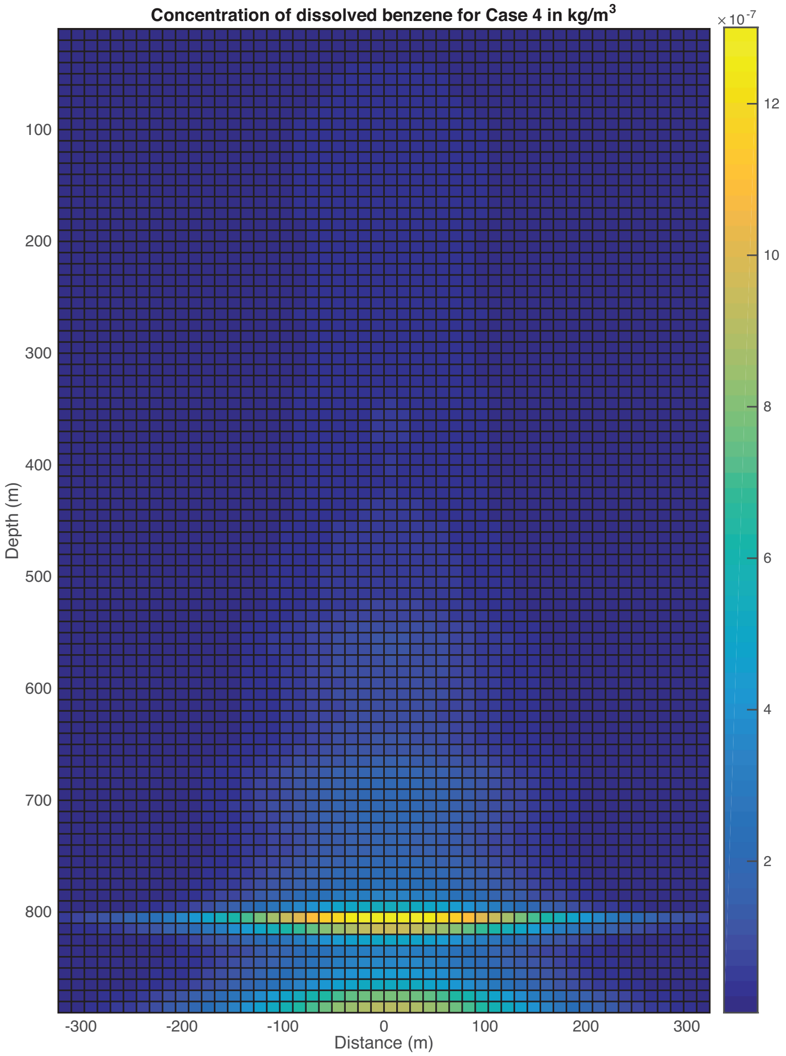

FIGURE E.19 Concentration of benzene for Case 4 on a plane 10 km downstream of the *Deepwater Horizon* wellhead and normal to the crossflow.

Figure E.19 shows a sample result from the simulation matching the parameters of Case 4, our best-case hindcast simulation, for benzene. In order to capture the input from each of the modeled bubbles and droplets, we make the calculation at a distance $x = 10$ km downstream of the *Deepwater Horizon* wellhead. The colormap in Figure E.19 shows the computed concentrations on the yz-plane normal to the currents at this location.

The currents change direction with height, and at each depth, we assume that all bubbles are aligned on a single x-axis, parallel with the currents. Figure E.20 plots the currents we used for all our simulations, which were measured near the *Deepwater Horizon* wellhead by a near-surface, down-looking acoustic Doppler current profiler (ADCP) (Gros et al., 2017). Our assumption that the particles are always aligned along the currents yields the largest prediction for the dissolved concentrations. Comparing to Equation (2), we also see that concentrations are maximum where the dissolution $\dot{m}_i^{'}$ is large and/or where the currents U or the plume width σ are minimum. Because

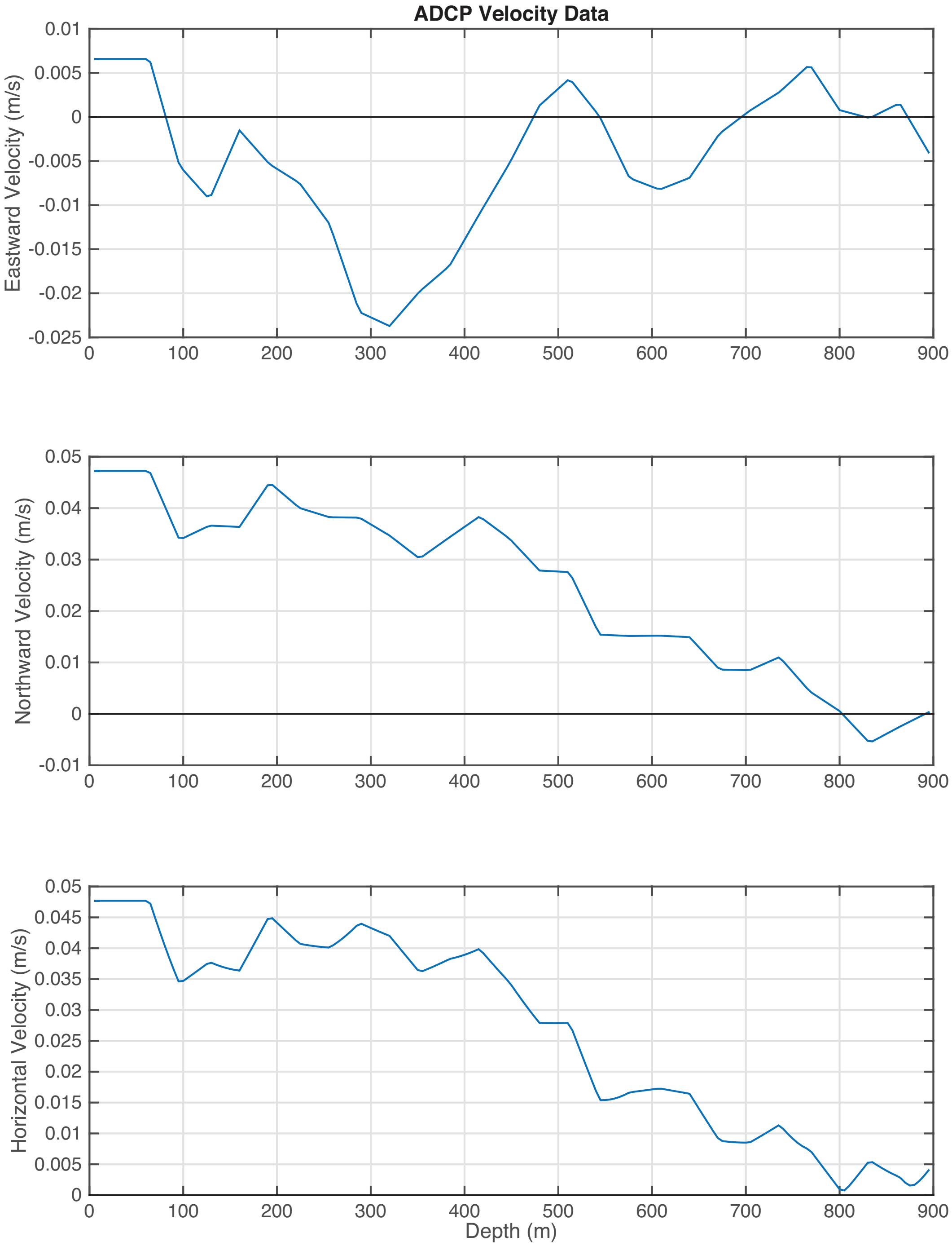

FIGURE E.20 Measured ocean currents near the *Deepwater Horizon* wellhead on June 8, 2010.

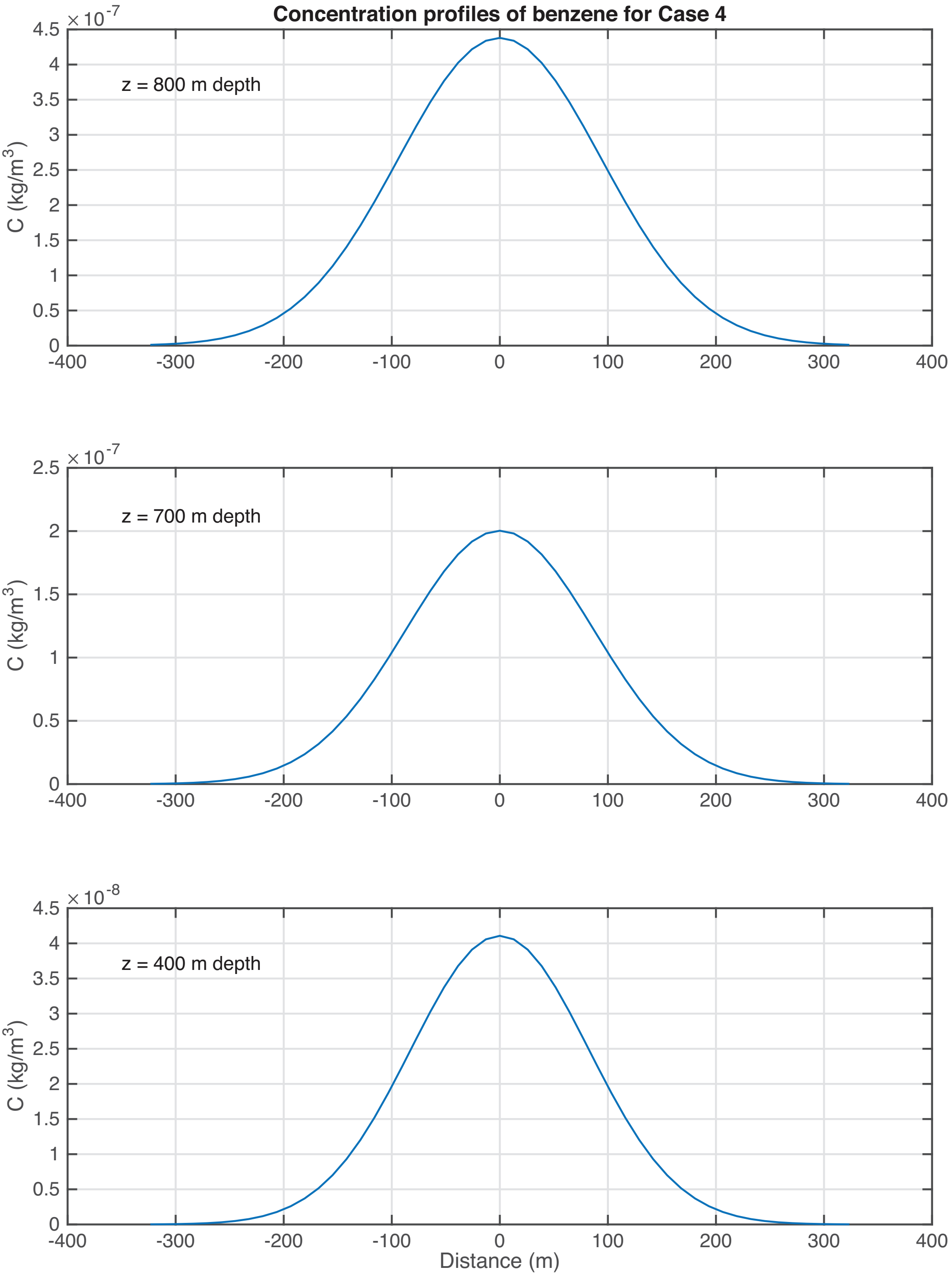

FIGURE E.21 Profiles of the concentration of benzene for Case 4 at a location 10 km downstream of the *Deepwater Horizon* at three different depths, and along lines normal to the crossflow. Note that different *y*-axis scales are used to make the plots readable.

this is a steady-state solution, concentrations increase as $U \rightarrow 0$, and because $\sigma \approx \sigma_0$, the plume width is fairly constant. Based on these behaviors and Figure E.20, we expect the highest concentrations near the intrusion, where the currents are minimum and the oil and gas is the freshest (least weathered). The distribution of concentration in the map agrees with these expectations.

In Figure E.21, we present the profiles benzene for Case 4 at three different depths at a distance of $x = 10$ km downstream of the *Deepwater Horizon* wellhead, hence, profiles extracted from Figure E.19. Peak concentrations occur low in the water column, close to the intrusion layer, and are on the order of 10^{-7} kg/m^3 (10^{-9} mol/l) over a slice about 400 m wide. The width of the concentration cloud is also largest at 850 m depth and decreases slightly with height. The narrower concentration plume at shallower depth is due to the currents: Oil droplets advect farther downstream at shallower depths; hence, the dissolved plume experiences less lateral diffusion between the location where the droplets are dissolving and the plane at 10 km downstream where the concentrations are evaluated as the depth reduces. The peak benzene concentrations also decrease with decreasing depth, dropping to 10^{-8} kg/m^3 (10^{-10} mol/l) over a slice about 300 m wide at 400 m depth.

Similar behavior is observed for each of the dissolving components, with the values of the concentration depending on the solubility of each component in the Lagrangian bubbles and droplets as their compositions evolve with height. The properties of the 279 pseudo-component oil model as well as results of each of these concentration calculations in the form of ascii text files are included in the digital appendix to this report.

8. Discussion

Herein, we have reported the results of our TAMOC simulations for the *Deepwater Horizon* accident on June 8, 2010, for six different prescribed subsea dispersant application rates and bubble and droplet size prediction models. We had previously reported the results of Cases 2 (no subsea dispersant injection) and 4 (reported subsea dispersant injection) using VDROP-J to predict bubble and droplet size distributions in our *PNAS* paper (Gros et al., 2017). Here, we also simulated a new case, Case 7, in which VDROP-J is used to predict bubble and droplet sizes for a theoretical optimal subsea dispersant injection rate of 1% DOR.

Figure E.22 compares the results of these three cases in the format of Figure E.2, together with the observed data. This figure shows that, using our model, Case 4 gives a prediction that is closest to the observations, and Case 7 predicts that a significantly greater proportion of the released petroleum would have been sequestered in the ocean within a radius of 10 km of the *Deepwater Horizon* wellhead had a higher DOR been applied subsea. From Figure E.18 for Case 7, 52% of the released petroleum would either be dissolved in the intrusion layer or the water column or suspended as small droplets in the subsurface intrusion. Figures E.9 and E.6 show that the actual DOR used during *Deepwater Horizon* is predicted to have sequestered 27% of the released petroleum (Case 4), and that if no dispersants had been used, 22% of the released petroleum would have been sequestered (Case 2).

These different dispersant injection rates also change the concentrations of light petroleum hydrocarbons in the mid-ocean water column. In Figure E.23, we plot the maximum concentration of benzene between the intrusion layer and sea surface at 10 km downstream of the broken Macondo wellhead for these cases using our new method in Section 7. The maximum concentrations are computed at $y = 0$ in Equation (2) and plotted as a function of depth z. The differences between the baseline case of 0.4% dispersant injection (Case 4) and no-dispersant (Case 2) are about an order of magnitude throughout the water column, with Case 4 having higher concentrations due to the larger amount of benzene dissolution with dispersant injection. The 1,000-fold reduction in atmospheric benzene emissions between these two cases results from the integral of this order-of-magnitude difference in benzene concentration over the full water depth. Similarly,

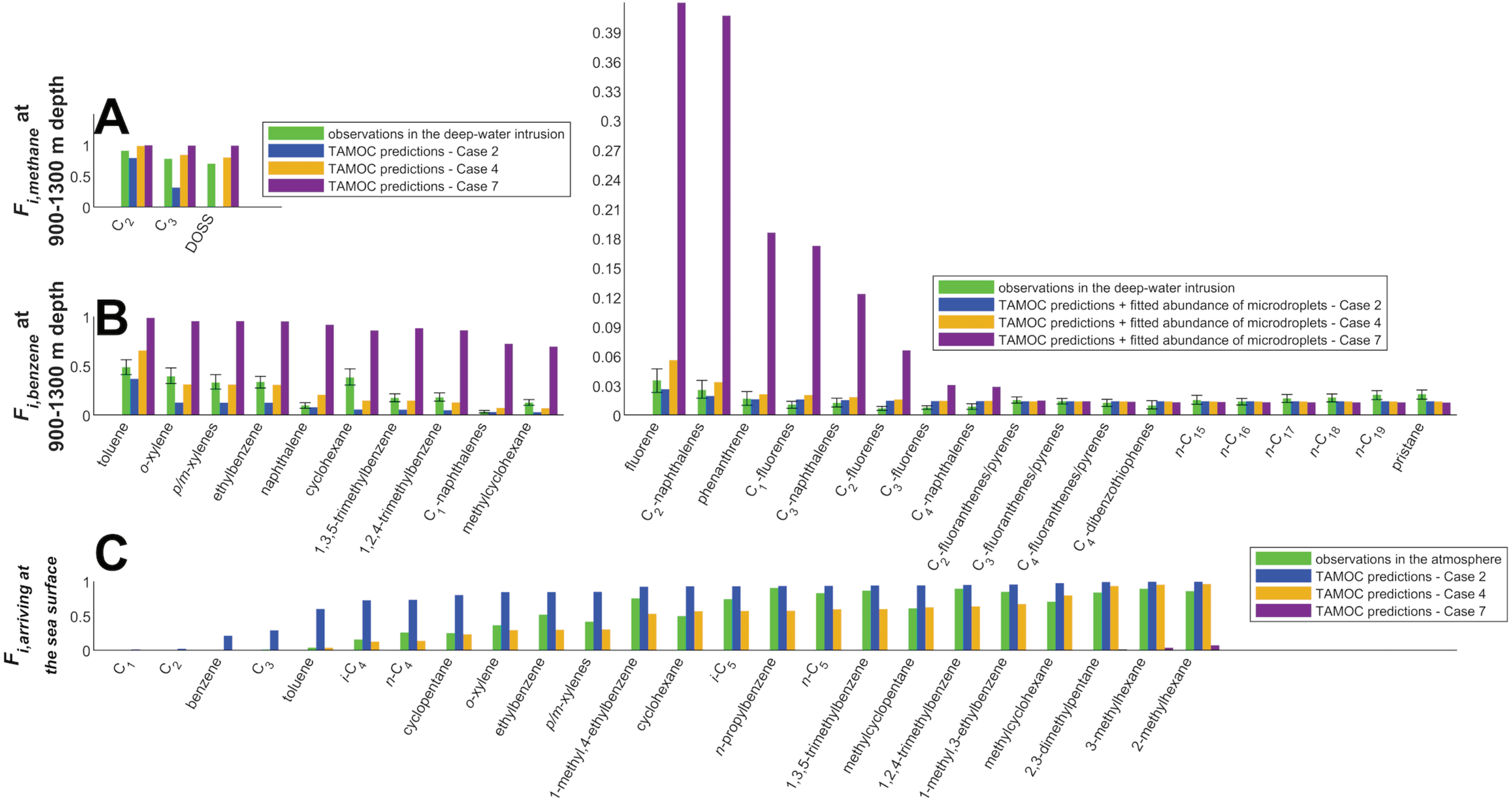

FIGURE E.22 Comparison of the simulation results for Cases 2, 4, and 7.

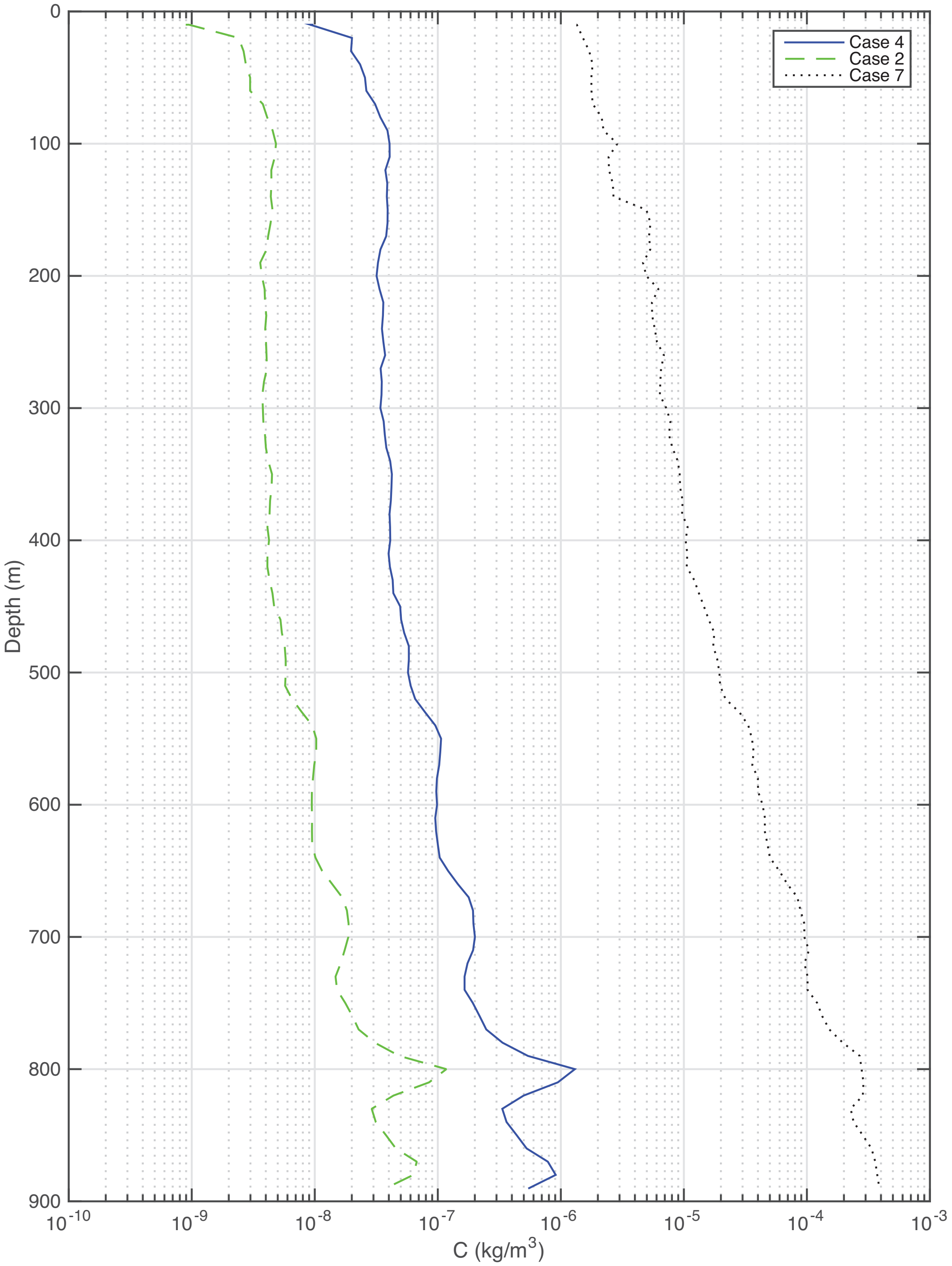

FIGURE E.23 Vertical profiles of the maximum dissolved benzene concentration for Cases 2, 4, and 7 at a location 10 km downstream of the *Deepwater Horizon* wellhead.

Case 7, with 1% dispersant injection, results in even greater benzene dissolution through the water column and nearly two orders-of-magnitude higher benzene concentration in the mid-ocean water relative to the baseline, Case 4. All of these benzene concentrations remain small, however, with maximum values less than 4×10^4 kg/m^3 (5.1 μmol/l, or 0.4 parts per million).

The results for Cases 2 and 4 show that the actual amount of petroleum reaching the sea surface is fairly similar with and without subsea dispersant injection for the DOR used on June 8, 2010 (73% with subsea dispersant injection and 78% without). However, as we show in Gros et al. (2017), the composition of the surfacing petroleum is quite different due to the different dissolution occurring for the smaller droplets with dispersant injection. We previously reported that the mass flow rates of C1-C9 VOCs to the atmosphere reduced by 28% between Cases 2 and 4, and that the mass flow rate of the compound benzene reduced by 2,000 times with subsea dispersant injection (Case 2 compared to Case 4).

Similar results for other cases simulated here can also be extracted from the model results. Comparing the optimal DOR of 1% (Case 7) to the case of no dispersant injection (Case 2), we predict a reduction of C1-C9 VOCs of 84%, and that no benzene reaches the sea surface (e.g., infinite reduction of benzene mass flow rate to the atmosphere). Likewise, if we compare Case 1 (maximum possible droplet size) to Case 2 (VDROP-J no dispersant case), the flow rate of C1-C9 VOCs differs by only 10% (Case 1 being higher), and the benzene mass flow rates differ by 2.6 times (Case 1 being higher). If we compare Case 5 (droplet sizes following partial dispersant mixing) to Case 2, C1-C9 VOC emissions are reduced by 30% in Case 5 and benzene emissions reduce by two times. Hence, for the partial dispersant mixing model of subsea dispersant injection, one would not conclude that dispersants significantly affected atmospheric concentrations of VOCs. Finally, comparing Cases 6 (C-IMAGE size distribution) to Case 2, C1-C9 VOC emissions are reduced by 66% and benzene mass flow rate to the atmosphere is nearly suppressed (3×10^6 times reduction). This is similar to performance of the optimal subsea dispersant injection predictions using VDROP-J at 1% DOR.

Because the three Cases 2, 4, and 7 are all based on the same model assumptions and because Case 4 gives the best match between the model predictions and the observations, these cases may be considered as reliable predictors for the effect of subsea dispersant injection on the Macondo oil during the *Deepwater Horizon* accident. The DORs used during the accident were lower than optimal, but resulted in some liquid oil not reaching the sea surface and significantly improved air quality by suppressing atmospheric emissions of VOCs by 28%, including a 2,000 times reduction of benzene emission. Had a higher DOR of 1% been used, our model predicts that significantly more liquid oil would have remained subsea within the 10 km radius we have studied surrounding the *Deepwater Horizon* wellhead, atmospheric emissions of VOCs would have reduced by 84% relative to the no-dispersant case, and benzene emissions could have been entirely suppressed.

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APPENDIX F

META-ANALYSIS OF AQUATIC TOXICITY DATA

DATA COMPILATION

A meta-analysis of aquatic toxicity data from laboratory exposures with whole organisms was undertaken to better understand the effects of dispersants and of physically and chemically dispersed oil. While the quality of toxicity data varies considerably across studies, selection of data included in this meta-analysis followed a strict set of rules aimed at selecting the best available information. These rules followed those used to develop the Chemical Aquatic Fate and Effects (CAFE) database, which contains aquatic toxicity for dispersants as well as both physically and chemically dispersed oil (Bejarano et al*.,* 2016; NOAA/ERD, 2015), and included:

1. Data from original scientific publications and peer-reviewed literature (primary source) rather than from reviews or unverifiable sources;
2. Studies clearly stating the species' common and/or scientific name, oil source, and dispersant name used in toxicity tests;
3. Studies with complete descriptions of biological test methods, or referencing an appropriate published method;
4. Acceptable effects endpoints relative to control tests, with inclusion of studies that do not discuss or mention the use of controls considered on a case by case basis; and
5. Analytical methods for chemical characterization described or referenced; only toxicity data reported as measured concentrations are included.

Data from studies published between 2005 and 2012 were queried directly from CAFE, while studies post-2012 were identified via online searches or direct contact with researchers in the field. Priority was given to papers reporting toxicity for both water-accommodated fraction (WAF) and chemically enhanced water-accommodated fraction (CEWAF) for the same oil and under the same testing conditions. In addition, this meta-analysis included Natural Resource Damage Assessment data from the *Deepwater Horizon* oil spill collected by the *Deepwater Horizon* Natural Resource Damage Assessment Trustees, with most data queried from a public data repository (DIVER, 2017). All references and data sources included in this meta-analysis are provided below. For the purpose of this meta-analyses, only median lethal and median effects concentrations (LC50 and EC50, respectively) were included, and to the extent possible, information on testing approaches was tabulated and summarized. In all cases, toxicity data reported with qualifiers or displayed in figures but not reported in the text were excluded from these analyses. Because of the narrow focus of this meta-analysis, only chemically dispersed oil prepared with select dispersants for which stock piles are currently available (i.e., Corexit® 9527, Corexit® 9500, Finasol® OSR 52, Dasic Slickgone, Accell Clean) are included. Dispersant-only toxicity data from a recent meta-analysis (Bejarano, 2018, and references herein) that followed a similar approach to the one described above were used in assessments on the relative toxicity of the dispersants listed above. Unlike toxicity data for WAF and CEWAF, most dispersant-only toxicity data are commonly reported as nominal concentrations; thus, all nominally reported dispersant toxicity data were used in these analyses. For consistency with the WAF/CEWAF meta-analysis, dispersant-only toxicity data focused on the select dispersants mentioned above.

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