

Understanding Marine Oil Spills: Improving Decision-making and Identifying Research Needs

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The authors declare they have no actual or potential competing financial interests.

Abstract

The extensive and catastrophic potential faced in responding to oil spills highlight the need for transparent decision-making, rapid action, and effective communication. Here we present a framework for understanding the environmental management decision-making process based on a critical review of the existing oil spill response literature. This framework identifies key variables that influence the fate of a marine oil spill. Future research needs are identified and response technology options are clarified with the aim of minimizing the impact of such a spill on the ecosystem. In addition to technological improvements, the need for baseline data collection and rapid decision-making is highlighted by a case study of a 2011 oil spill in the Bay of Plenty, New Zealand.

Key Words: Oil spill, decision-making, marine ecosystem, review

1. Introduction

Fossil fuels are a cornerstone of modern human society, and despite promising developments in alternative energy sources, the extraction and use of oil is projected to continue to grow by at least 25% over the next 25 years [1]. With the reliance on oil for energy comes the risk of accident. Recent history contains many examples of oil release into the environment, including many high profile incidents with far-reaching consequences. These large oil spills are less numerous than small spills, but they publically showcase the political, economic and ecological complexity of spill cleanup [2-5]. Historically, many spills have been the result of damage to tankers, such as the *Torrey Canyon* spill in 1967, the *Amoco Cadiz* spill in 1978, the *Exxon Valdez* spill in 1989 [6], and the recent MV *Rena* spill in 2011 [7]. As easily accessible resources are

depleted, drilling is moving offshore, leading to underwater well blowouts such as the *Ixtoc I* blowout in 1979 and the *Deepwater Horizon* blowout in 2010 [8, 9]. Extraction is also occurring in even more extreme environments; as the recent grounding of the *Kulluk* in December 2012 made clear, this could lead to potentially even greater catastrophes in the event of an oil release [10]. Both tanker and wellhead oil spills can result in substantial release of oil in areas that are both environmentally sensitive and have an impact on human health and well-being [8]. This contributes to loss of lives and capital, and to the deterioration of the health of surrounding ecosystems [11, 12] and the services they provide to adjacent communities [13].

Study of previous oil spills [6, 14] and

implementation of corresponding safeguards helps reduce the impact of future spills. Many organizations have resources that outline comprehensive spill response plans [15-18]. However, the complexity of the challenges and the variety of stakeholders involved highlight the need for transparent decision-making that is based on clear answers to key questions [19].

Stakeholders invested in addressing an oil spill often struggle to identify and communicate available resources, and potential responses. To facilitate this communication, our review is organized around a five-question framework. These identify important decision points to consider during an oil spill in an offshore marine environment. We conducted a broad review of technical reports, information from government agencies, media accounts, and peer-reviewed literature. This approach led to in-depth reviews of oil composition and fate, spill response technologies, and environmental impact and recovery. Studies that incorporate available knowledge and identify key decision points serve to prepare responders for future spills and communicate available options [19, 20].

In addition to effective responses to oil spills, it is essential to minimize unintended stress on the ecosystem created by cleanup efforts. Oil spills can create large-scale disruptions of a marine ecosystem [21, 22], and subsequent disturbances may further decrease ecosystem resilience [11, 23, 24]. From our review of the literature we found that environmental baseline data is critical for optimal use of available response technologies when a spill occurs and for accurate assessment of ecosystem recovery. Unfortunately, systems are often not in place to gather this data at active or potential future drilling sites.

We demonstrate the potential benefits of examining oil spills through this environmental management framework by considering the

response to a recent oil spill incident in the Bay of Plenty, New Zealand. This example uses a relevant scenario to demonstrate many of the key findings of this review. We then suggest technical improvements to existing responses and emphasize the importance of collecting environmental baseline data at drilling sites, highlighting areas of research and response where actions can be taken *now* to minimize ecosystem stress in future spills.

2. Key Variables Affecting Successful Oil Spill Response

The ultimate goal of a successful oil spill response is to support ecosystem resilience, which is the capacity to absorb disturbance and to reorganize while undergoing change, so as to still retain equivalent function, structure, identity, and feedback networks [25]. Toward this end we have outlined the essential variables to be included in an environmental management plan that will help coordinate and direct response efforts [24]. Awareness of ecosystem resilience and of the synergistic effect of perturbations is key to the assessment of possible interventions and to the selection of an environmentally preferable response [23]. Our review does not address financial and political costs of the possible options; rather, estimations of the environmental damage [26] and the effects on the local ecosystem [12], including the human population, are emphasized.

In order to understand the key variables that inform oil spill responses, we used existing public resources that outlined spill response plans [15-18, 27-29], available literature on existing technologies [30-38], and emerging case studies of the *Deepwater Horizon* incident [8, 19, 20, 39-44], as well as available case studies from older incidents [14].

Using this understanding of response technologies, we identified key questions that must be asked when a spill occurs in order to

facilitate rapid implementation of an appropriate response. We narrowed the field of parameters by considering a number of possible spill scenarios and determining the physical, chemical and biological factors that are likely to have an effect on the eventual response effectiveness. These variables are broken down into three subsections: the first addresses the properties of

the oil itself and the nature of the spill (Figure 1: yellow), the second environmental and ecosystem conditions (Figure 1: blue), and the third available response technologies (Figure 1: orange). The five key questions can clearly communicate the treatment options and decisions to all stakeholders.

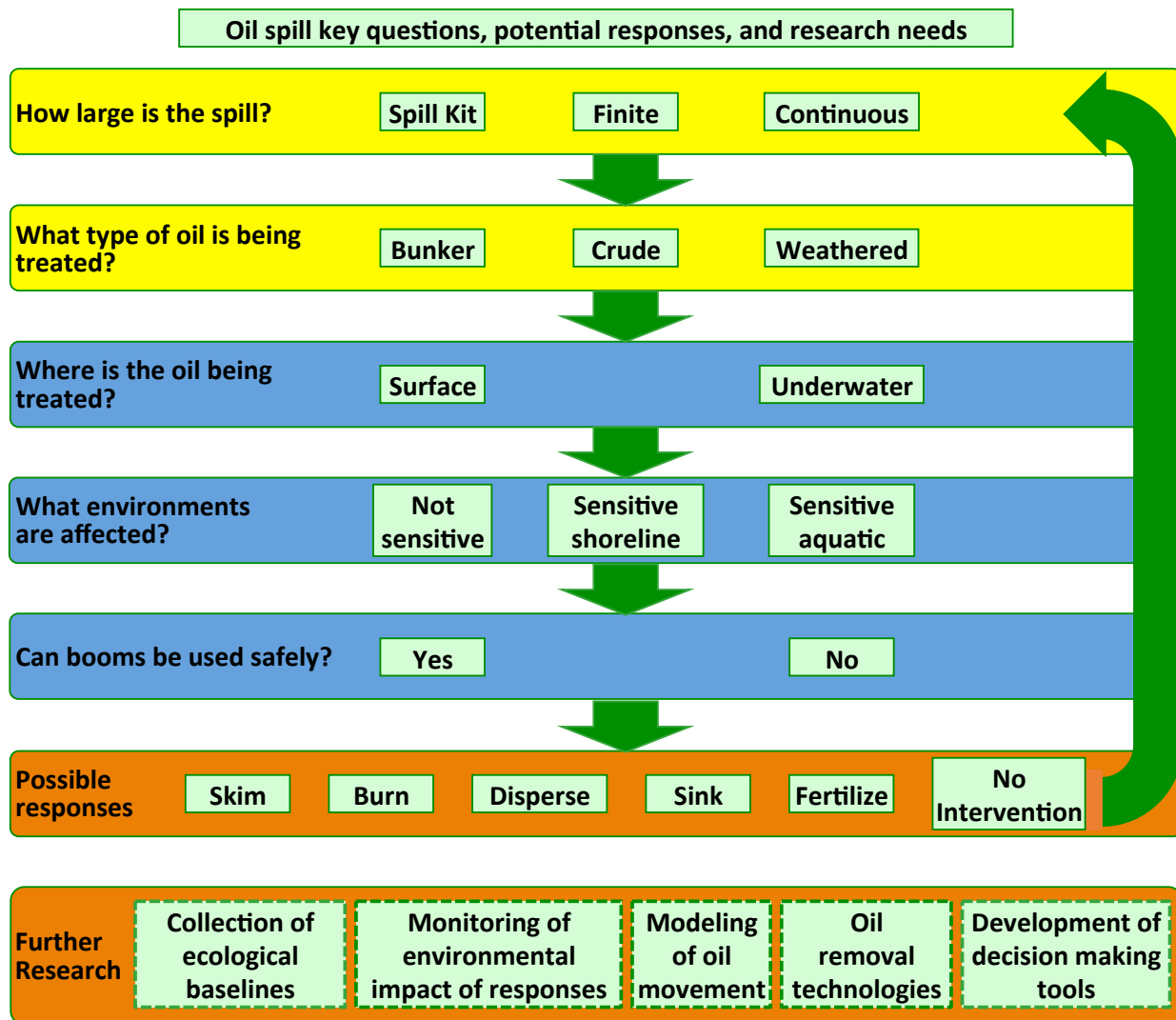


Figure 1. Potential responses to an oil spill based on key decision-making questions. The outline guides the user through a series of questions about the spill (yellow), the physical and biological environment in which the spill occurs (blue), and potential cleanup responses (orange).

Because an oil spill is not static and evolves over time, a single analysis of the situation is rarely sufficient. In some cases the answers to each

question will change because of cleanup efforts undertaken; in other cases the optimal response may be affected by changes in weather patterns,

the amount of oil spilled (as in a continuous release scenario), or new information about the sensitivity of surrounding environments.

2.1 Oil and Spill Properties (Figure 1: Yellow)

The size of an oil spill and the type of oil spilled define the scale of the spill and influence the types of responses to be considered.

2.1.1 Spill Size

The size of an oil spill has a strong correlation to the complexity of the response required. In broad terms, oil spills may be classified either as being very small, large with a fixed volume from a single release, or large with a continually changing volume due to ongoing release of oil into the environment. The response to a large spill is multi-faceted and will evolve substantially over the course of a cleanup operation.

On a very small scale (< 100 gallons) it is often possible to completely contain and remove spilled oil with absorbent materials, such as those in the “spill kits” frequently found onsite in ports [45]. With larger spills, such a straightforward response does not suffice for oil removal; it is in such cases that responders must identify all options available for cleanup.

Approximately 55% by volume of the oil spilled in navigable waters in the United States comes from vessels of various types (barges, tankers, freighters, and other watercraft) [16]. The total possible volume of oil from a vessel is limited by the carrying capacity of the vessel. The carrying capacity of tankers, for example, ranges from 10^6 to 10^8 gallons, although the likelihood of a large, full tanker spilling 100 million gallons of oil is very low [46, 47]. If oil is leaking slowly from the vessel, the actual amount of oil in the water may be continually changing, but the finite upper bound on the amount of oil being treated is useful in planning a cleanup response that will span over a longer period. In any situation where a leak is ongoing, it is essential to prioritize

stopping the continued release of oil in the cleanup strategy, since oil is much easier to remove before coming into contact with environmental media.

Offshore production facilities (stationary spill sources other than pipelines) account for 13% by volume of the oil spilled in water in the United States; pipelines account for the remaining 31% of spills in navigable waters [16]. Spills on navigable waters in recent US history have ranged in size from very small, with 94% of the total number of offshore production spills measuring 2100 gallons or less [48], to the nearly 5.0 million barrels (210 million gallons) released in the *Deepwater Horizon* disaster [19, 49]. When oil is released from a wellhead or a pipeline, there is no clear upper limit on the amount of oil that will be released until the flow is successfully stopped. However, even if emergency procedures to stop the flow of oil are unsuccessful, it is essential to concurrently initiate a dynamic cleanup plan to respond to the rapidly changing conditions caused by the continuous influx of oil.

In both vessel and wellhead or pipeline spills, it can be very difficult to accurately quantify the oil released into the environment [50]. While such values are important for long-term environmental impact analysis, difficulties in estimating the exact amount of oil released into the environment must not paralyze decision-making and cleanup efforts. It is sufficient to provide an order-of-magnitude estimate that informs how resource-intensive a response will be and allows decision makers to evaluate the adequacy of their resources.

2.1.2 Oil Type

The composition of oil that is spilled strongly influences the available response options. Oil can be broadly categorized as one of three types: crude oil, bunker fuel or weathered oil. Crude oil is the mixture of hydrocarbons that has been

extracted from a well and is being transported to a refinery. Bunker oil is primarily used to power marine equipment. Weathered oil results from the exposure of spilled oil to environmental conditions for any period of time, resulting in evaporation of the lighter constituents and partial emulsification.

Crude oil accounts for approximately 29% by volume of the total oil spilled on water globally [16], while spills of bunker fuel comprise 48% by volume of the total oil spilled on water [16]. (The remaining 23% is a combination of waste, mixed oil, and refined products). While the exact composition of crude oil depends on the source, it generally consists of a mixture of lighter (C_{4-16}) and heavier saturated hydrocarbons (C_{17} and greater), various aromatic and polyaromatic hydrocarbons, and small amounts of

asphaltenes, resins, and waxes [16, 51, 52]. When fresh, it generally floats on calm water and forms a slick.

By contrast, bunker oil is composed primarily of heavier saturated hydrocarbons, asphaltenes, resins, and waxes, and contains few light components, making it much more viscous than crude oil. Bunker fuel spills also tend to be smaller in volume, although their frequency is higher: the *Cosco Busan* spill in the San Francisco Bay epitomizes bunker oil spills with a volume of just over 50,000 gallons [53]. Table 1 provides compositional breakdowns of South Louisiana Crude (a typical example of a light crude oil) in the form that it is transported and in the form that it initially leaves a wellhead, and of Bunker Oil C, which is the predominant form of fuel oil used.

Table 1. Compositions of South Louisiana Crude (in a surface spill and at the wellhead) and Bunker Oil C [43, 54].

Component	South Louisiana Crude in Transport (% weight)	South Louisiana Crude at Wellhead (% weight)	Bunker Oil C (% weight)
CH ₄	0	20	0
C ₂₋₄	4.7	11	0
C ₅₋₈	16	12	0
C ₉₋₁₆	16	12	3.5
C ₁₇₋₄₁	44	33	39
BTEX ^a	3.4	3.8	0.2
PAH ^b	0.9	1.3	2.9
Other Aromatics	8.3	4.4	26
Resins	5.9	4.4	16
Asphaltenes	0.8	0.6	13
Waxes	1.7	1.3	2.5

^aBenzene, toluene, ethynylbenzene, and xylenes. ^bPolyaromatic hydrocarbons

The composition of spilled crude oil changes due to evaporation, wave action, and exposure to sunlight and microbial activity [38, 40, 55]. The rate at which all of these factors act can vary [54], but the effects are easily observed by

quantifying the composition of weathered oil. Evaporation and microbial activity, both of which depend on temperature, generally remove lighter components of oil, which results in increased viscosity, decreasing the effectiveness

of both skimming and dispersants [43, 52]. Over two days at 15 °C in a controlled study, 40% of crude oil evaporates; after this time the chemical composition of spilled crude oil is similar to that of bunker oil [16, 32, 33, 54]. By contrast, only 3% of bunker oil evaporates in the same time [16].

Turbulent water increases the degree of both dispersion and emulsification of oil; oil-water emulsions are much more difficult to clean up than oil itself. This was demonstrated in the *Torrey Canyon* spill, where lack of preparedness delayed initial cleanup of fresh crude oil off the coast of Britain, resulting in the weathering of this oil [56]. In general there are more options and the removal of oil is much simpler before significant weathering has occurred, underscoring the need for rapid response to oil spills. Knowledge of initial oil composition and the changes that occur with weathering is essential for effective cleanup. Characteristics such as volatility and viscosity will have a significant impact on the effectiveness of various technologies, such as the ability to allow for controlled burns or the effectiveness of skimmers.

2.2 Environmental Considerations (Figure 1: Blue)

The location of the spilled oil with respect to the shoreline, various aquatic ecosystems, and the ocean floor affects the selection of appropriate responses. The Environmental Sensitivity Index developed by the National Oceanographic and Atmospheric Administration (NOAA) [26] is presented here as a potentially useful rubric for evaluating environments that may be affected. Additionally, geographical and weather factors significantly influence the range of potential responses. Rather than enumerating all of the potential factors, it is possible to summarize their influence on potential spill responses by asking if booms can be used. While booms are a response rather than a direct environmental factor, they

emerged as an effective technology that, if available and possible to deploy, are often a beneficial first response since they both isolate the affected region and enable other treatment responses. This question encompasses physical and environmental factors, and informs the possibility of using several cleanup methods.

2.2.1 Surface/Underwater

This parameter considers the difference between oil that is released from a point on the surface of the water and oil that is released underwater, for example from a damaged wellhead. This parameter is very closely tied to the properties of the oil itself.

There are two significant differences between oil spilled on the surface vs. underwater: the initial composition of the crude oil (See Table 1), and the tendency towards natural dispersion vs. slick formation. Crude oil released from a wellhead has a larger contribution from lighter fractions, most notably a contribution on the order of 20% methane by weight [43]. The lighter components are more likely to float to the surface after an underwater release, while heavier components are more likely to remain suspended in the water column. However, lighter components dissolve easily in water and can become trapped in the water column [43]. When they do reach the surface, they may be significantly weathered. A study by Johansen et al. of a controlled underwater oil release demonstrates that the rate at which oil reaches the surface and the degree of weathering depends on a number of factors, including rate of release and size of the droplets released [57].

The response technologies available will change depending on the state of the oil once it reaches the surface, since not all technologies will work with weathered oil. Additionally, the fate of oil that remains trapped in the water column needs to be considered in the response [58-60]. Many technologies are designed for surface oil and

cannot be used underwater.

2.2.2 Environmental Sensitivity

Given that oil spills occur in a diversity of ecosystems, it is necessary to quickly evaluate the affected area and the potential environmental impact of the spill. Based on a combination of situational factors, such as predicted weather, local currents and tides, natural degradation rate of oil, and water temperature, responders can evaluate whether nearby sensitive environments are likely to be affected by the spill or by any proposed treatments. A set of credible guidelines for classification and identification of habitats has been created by NOAA as part of their Environmental Sensitivity Index (ESI) mapping system [26]. This tool is a set of multilayered

maps of shorelines of the United States, generated from digital databases using Geographic Information Systems (GIS) to which a sensitivity classification has been applied [26, 61]. An ESI map contains information on biological resources, human-use resources, and a shoreline classification and rank. The shoreline classification and rank integrates four factors: exposure to wave and tidal energy, shoreline slope, substrate type, and biological productivity and sensitivity. Rankings range from 1 to 10E (see Table 2) and provide a clear, increasing scale of relative sensitivity to contact with oil, with a higher ESI code corresponding to a more sensitive habitat [62]. Although it is composed of several quantitative components, the overall ranking is qualitative and guides the establishment of protection priorities.

Table 2. Environmental Sensitivity Index shoreline classification for Estuarine Ecosystems. The contents of this table are reproduced with permission from NOAA [26].

ESI Code	ESTUARINE ENVIRONMENTS
1A	Exposed rocky shores
2A	Exposed wave-cut platforms in bedrock, mud or clay
3A	Fine- to medium-grained sand beaches
4	Coarse-grained sand beaches
5	Mixed sand and gravel beaches
6A	Gravel beaches
7	Exposed tidal flats
8A	Sheltered scarps in bedrock, mud or clay & sheltered rocky shores (impermeable)
9A	Sheltered tidal flats
10A	Salt- and brackish-water marshes
10B	Freshwater marshes
10C	Swamps
10D	Mangroves
10E	Inundated low-lying tundra

This shoreline classification system [26] can be the foundation for determining the sensitivity of an affected environment. Although the NOAA maps are specific to the United States, comparable maps have been created for the

coast of the United Arab Emirates [63], the Loire estuary in France [64] and the Coatacoalcos and Tonalá Rivers Low Basin in Mexico [65]. Comprehensive sensitivity assessment for a specific environment surpasses the level of detail

that can be provided by the ESI, but the classifications and ranks found in ESI guidelines for shoreline environments present an excellent framework for rapid estimation of the sensitivity of potential marine environment affected.

2.2.3 Use of Booms

An oil spill can be treated or removed more easily if it is prevented from spreading. Booms are floating barriers used to contain and localize the oil at the water's surface [31]. A typical boom consists of a length of fabric filled with buoyant material (e.g. polypropylene) to keep one side afloat, with a heavy chain or weight attached to submerge the other side. The floating side is designed to prevent oil from spilling over, whereas the submerged side is made to prevent oil from seeping under the boom. Some booms contain hydrophobic material or oil sorbents, which not only contain but also help remove the oil from the water. Recent advances in nanotechnology have made more selective sorbents from hydrophobic nanowires that enhance oil-water separation [66, 67]. Although not a complete response on their own, booms enable a number of potential responses, including skimming and burning [31].

Weather is the primary factor in determining the feasibility of boom use, because calm seas are required for booms to be effective; currents of greater than one knot and waves higher than two meters typically deter the use of booms [14, 68, 69]. The existence of the oil as a surface slick is also a prerequisite. Consequently, asking if booms can be used determines several important factors. In practical terms, the availability of booms and boats from a location close enough to the oil spill that they can be applied quickly should also be considered. In the event that complete containment or cleanup of oil is not possible, booms can also be used as a protective barrier for sensitive environments; in

the *Exxon Valdez* spill, for example, booms were used to protect a salmon hatchery [7, 53, 70].

2.2.4 Additional Environmental Factors

Temperature and weather conditions can affect the viability of an oil spill response. These factors inform several of the key questions that we have identified (such as weathering and use of booms); because of this we chose not to represent them as separate questions. Substantial movement of spilled oil, either due to weather or from underwater currents, affects the spatial distribution of the oil [58-60, 71-73]. This effect of weather and sea conditions on oil movement must be considered when determining which ecosystems are potentially impacted. Water temperature impacts the rate of evaporation of oil in a roughly linear manner [54] and also affects the metabolic activity of microbial communities that assist in the natural biodegradation of oil [32, 33]. These factors also determine the timeframe during which burning (which requires the presence of volatile components) and fertilization are applicable. In addition, strong winds, storms, and turbulent water can drastically change the conditions at the surface of an oil spill, making responses that require containment booms impractical.

3. Existing Responses and Technologies

Once the chemical and environmental factors affecting the spill are considered (Figure 1), there remain a number of possible responses (see Table 3 and Figure 1: Orange). These are not necessarily to be used in isolation; the complex and dynamic nature of a spill will often demand a combination of responses as the spill evolves. While its mention in the literature is rare [24], the option of not intervening should also always be considered, as it can sometimes avoid causing greater harm to the impacted environments. Table 3 outlines many of the potential response strategies that can be employed along with their advantages and disadvantages.

Table 3. Summary of existing oil spill responses.

Response	Description	Advantages	Disadvantages
Skimming	Machines that use sorbents or vacuum to remove oil [31]	Permanently removes surface oil	Cannot be used in rough weather or if spill is inaccessible by boat Only works with surface oil Difficult with emulsified oil Oil waste must be managed
Burning	Ignition and burning of surface oil	Can remove a large amount of oil in a short time One-step cleanup process	Must occur soon after the spill [74] Difficult with emulsified oil Requires booms for containment and surface thickness of >2mm [16] Creates air pollution [16]
Dispersants	Chemicals added to prevent oil slicks and lower local oil concentration	Reduces surface fire hazard Can make oil more accessible for natural degradation	Does not remove oil from the ecosystem Can be more toxic than the oil itself, or increase the oil toxicity by making it more bioavailable [34, 36]
Sinking	Sorbents that absorb oil and sink it to the sea floor	Removes oil from the surface Agents are chemically inert	Does not remove oil from the ecosystem Sorbents may leak over time [30] Toxic for sea floor life Banned in most countries [16]
Fertilization	Addition of nutrients to promote natural degradation	Can increase rate of natural oil degradation Can be oil soluble; keeps fertilizer at spill site	An effective ratio of fertilizer to oil can be difficult to predetermine [37] Untested effectiveness on weathered oil [35]
No intervention	Allow for natural degradation of the oil	Lessens further stress on ecosystem from intervention Minimizes effects of added chemicals	Can be slow and unpredictable Possible increased presence of oil slicks, and accompanying fire hazard and toxicity

3.1 Skimming

Skimming physically removes oil from the surface of the water. Booms are often required for skimmer operation; skimming is therefore limited by the same environmental conditions that affect boom use. Since skimmers can only operate at the surface with fresh oil that easily flows in a thick layer, skimming is ineffective for oil located underwater, for dispersed oil, and for weathered, emulsified, or extremely viscous oil [16].

Skimmers are rated by the speed and efficacy of oil removal, where efficacy is defined as the percentage of oil contained in the removed residue. These efficacy values can vary widely with the type of skimmer, the weather and sea conditions, and the type of oil, in addition to many other physical parameters such as temperature and slick thickness [16, 75]. The most efficient skimmers working in ideal conditions are 80-90% effective, but drop to 5-10% effectiveness in poor conditions [16].

While skimmers remove oil from the aquatic environment, they do not provide a permanent storage or disposal solution. The recovered oil must be initially stored in tanker ships, meaning these ships must be able to access the area of the spill. During the *Exxon Valdez* spill, this transfer of oil from temporary to more permanent storage proved difficult and delayed the cleanup [76]. Ultimately the oil must be reused or disposed of elsewhere, and a storage and disposal plan is needed when considering skimming as a cleanup response [77].

3.2 Burning

Burning oil on the surface of the water after an oil spill, also called *in situ* burning, is a common process used to clean up oil spills. This process can typically remove large amounts of oil (80,000 gallons/day), with up to 98% of the initial oil removed [16]. This response was used during the *Deepwater Horizon* spill, where 411 total burns removed 5% of the oil released - a total of 11.14 million gallons of oil [78]. Containment with fire-proof booms to maintain slick thickness and control of the flame is necessary, since an uncontrolled fire could endanger workers. Burning must begin soon after a spill occurs, before the lighter components of the oil have evaporated. Ignited fuel from a helitorch or bags with gelled gasoline can be added to assist ignition of oil slicks. However, for oil spills that contain bunker oil, weathered oil, or emulsified oil, such as the *Torrey Canyon* spill, ignition can be difficult and prevent burning from being a viable response [16, 30, 56, 78, 79]. By learning from burn responses to accidental oil spills as well as intentional burn studies, improvements have been made to increase ignition and burn efficiencies [80]. Compared to other cleanup processes where oil must be separated and discarded, burning is a one-step process. It also requires less equipment and fewer personnel, often making it appealing as a first response.

Burning is accompanied by obvious safety concerns and significant health risks. It is not recommended within 500 meters of populated areas because of the toxic substances and fine particulate produced by incomplete oil combustion [16]. For this reason, proper air quality monitoring is necessary when using this technique [81]. In addition, some states require prior approval to conduct burns, which may cut into the already short time window for effective burning, emphasizing the need for a pre-spill burn response plan so that quick action can take place [82].

Burning is a viable option when a quick and efficient cleanup is needed, especially if the spill threatens a shoreline. It should only be used when the fire can be kept under control, either with fireproof booms or natural barriers (e.g., marshes, frozen areas) [16]. Burning should not be used when watercraft are in direct contact with the spill. Often when there is a continuous oil spill and crews are actively working at the spill site, burning is not an option unless the oil slicks can be isolated from the source of the spill.

3.3 Dispersants

Oil spill dispersants are formulations of surfactants and solvents, used to lower local concentrations of oil and prevent large slicks from forming on the water surface. The surfactants are able to break up an oil slick and disperse the oil into small droplets [83]. The solvents act as a carrier for the surfactants, allowing the dispersant to penetrate the oil slick effectively. Dispersant use is intended to decrease the impact of large oil slicks that harm living organisms via direct contact, habitat damage, or disruption of food sources [84]. Dispersants must be used to treat fresh oil as soon as possible after a spill occurs, since weathering significantly decreases their effectiveness [85, 86].

The choice of which dispersant to use and how

much dispersant to apply depends on a number of factors, including oil type and amount, weathering, salinity, and temperature. Typically, dispersant is applied in a dispersant-oil ratio between 1:50 and 1:10, although some dispersants are recommended in ratios as high as 1:2. The United States Environmental Protection Agency, for example, currently lists 22 dispersants on their National Contingency Plan (NCP) Product Schedule, all of which have guidelines for application and data on toxicity and effectiveness [87].

Historically, dispersants were formulated with highly toxic aromatic solvents [88-90]. More recent dispersant formulations are much less toxic [90, 91], but the toxicity of the dispersed oil itself may be increased by greater bioavailability [34, 36, 92, 93]. Additionally, it has recently been shown that dispersants may persist in the environment after the oil has degraded [41]. The determination of dispersant toxicity is often limited to easy-to-measure endpoints such as LD50, which quantifies only acute exposure leading to death [94]. Toxicity can encompass many more variables, such as sublethal endpoints or effects resulting from chronic exposure [92, 95, 96], it may vary greatly between organisms, and it may not follow a linear dose-response relationship [97, 98]. While dispersants lower local concentrations of oil, they increase the geographic area where oil is detected [99, 100], meaning that the number of potentially exposed organisms is greater than for undispersed oil; this must be accounted for in decision-making processes.

Beyond toxicity, it is also extremely important to examine the effectiveness of dispersants [101]. Effectiveness depends on a number of factors, including type of oil, wave action, and water temperature [85, 86, 102]. There have been examples of oil spills where dispersant use has been highly effective, such as the *Sea Empress* spill in 1996 [103]. However, there have also

been spills where dispersants were applied and were largely ineffective because the oil was already weathered, such as the *Exxon Valdez* spill [6].

Dispersant application in the field is routinely monitored for effectiveness as well as toxicity [83], but very little field testing has been done outside of these emergency situations. However, in the event of dispersant application, follow-up studies can provide needed data about real-world effects. Unfortunately, this follow-up is rarely done, as in the case of the *Ixtoc I* oil spill in 1979. The response to this spill included one of the largest dispersant applications in history, but little is known about the long-term effects of dispersant in the spill area [94, 104].

The benefits of dispersant use include ease of application, effective removal of oil from the water surface, and prevention of slick formation by an underwater release [83]. Dispersant use can be merited in the event of a spill that threatens nearby sensitive shorelines or human life and cannot be treated by other means [27]. However, much of the literature is quite conservative about recommending dispersant use. Despite the potential benefits, dispersant use is still a controversial option.

3.4 Sinking

Sinking agents adsorb oil, making it denser and causing it to sink to the ocean floor. One example of a sinking agent is chalk (calcium carbonate), which is chemically and biologically inert [105]. Oil sunk to the ocean floor can only be biodegraded anaerobically, which is significantly slower than the aerobic biodegradation that can occur on the surface or in the water column [106]. However, there are advantages to rapid removal of oil from the water column; this response could be applied in an area where the ocean floor has minimal sensitive biota, particularly in an area where natural seeps occur and the ecosystem is

equipped for benthic oil degradation. One major risk associated with sinking is immediate damage to biota on the ocean floor, such as occurred in the 1971 blowout well blowout at Santa Barbara, where the benthic population was devastated from being coated with oil-soaked clay [107]. Similar wildlife destruction events in other cases where sinking agents were used has led to a complete ban on their use in many countries [16]. The long-term potential for leaching of oil back into the water may also be a risk, but the extent of this is not well documented.

3.5 Fertilization

Microbial communities capable of degrading oil are present in most marine environments, although they might be present at very low abundance [39, 108, 109]. Fertilization, also referred to as biostimulation, involves accelerating oil breakdown by indigenous microbes by adding nitrogen, phosphorus and other limiting nutrients to the spill. This technique can be used to treat oil slicks on water that remain after the bulk of the oil has been removed by skimming or burning.

Beach field tests during the *Exxon Valdez* spill indicated that assisted biodegradation could result in removal of 1.2% of total petroleum hydrocarbon per day [14, 39, 110]. Laboratory soil microcosm studies have reported that in unfertilized controls there is negligible hydrocarbon biodegradation; fertilizer addition significantly improves oil degradation within a few days [111-113]. Fertilization of ocean oil spills has been less well studied. However, the degradation activity of microbes at the oil-water interface has been enhanced by the addition of fertilizer [111]. Liquid fertilizers have been effective in *in situ* applications, such as in the 2002 *Prestige* spill off the coast of Spain. The oleophilic fertilizers used remained in the affected area and were shown to work well under high wave conditions [114]. A significant increase in biodegradation after fertilizer

addition has been reported for saturated and aromatic hydrocarbons, which make up the bulk of crude oil [39, 111]. Less conclusive evidence exists to support the practice of fertilization for resins, asphaltenes, and highly weathered oil [35, 114, 115].

Fertilizers must be added in an appropriate ratio and take into account baseline nutrient concentrations and release rate [37]. This highlights the importance of the acquisition of pre-drilling ecological baselines [9] and monitoring of the affected environment [116], as the addition of excess nutrients might lead to oxygen depletion in the ecosystem [37, 55]. Particular care should be taken in oxygen-limited environments and in those with lower nutrient levels, such as coral reefs, or in areas with low mixing rates and shallow waters, such as mangroves [27, 37]. In these environments it is critical to weigh the benefits of acceleration of biodegradation against potential further disruption of the ecosystem by nutrient addition.

3.6 No Intervention

Analysis of past oil spills reveal some scenarios in which the benefits of the oil spill response were minimal when taking into account the further stress and impact on the ecosystem caused by the response itself [24, 117]. With oil spills in coastal environments, such as coral reefs or mangroves, physical damage and trampling by cleanup workers has led to slower oil degradation and longer recovery times [27, 28]. Unfortunately this is usually recognized only in hindsight [28]. A recent synthesis of 240 studies surveyed ecosystems after anthropogenic perturbations, including oil spills, and found that the time to recovery increases with perturbation magnitude and as the number of disturbances increases [11]; this is a strong argument for considering non-intervention as an option in some spill scenarios.

Responders must often consider the tradeoffs of

a particular response. When considering the available interventions in situations involving sensitive environments, small spills of light oil, or inaccessible locations where physical damage to delicate structures is likely by workers or boats, the environmentally preferable response may be to allow the oil to degrade without further intervention, also referred to as monitored natural attenuation. In some areas, geographic conditions will lead to dilution and dispersion of the oil, and left alone, oil will evaporate, photo-oxidize and will biodegrade from naturally occurring hydrocarbon-degrading microbes. Experiments have shown that approximately 50% of typical light crude oil will evaporate within 20 hours [55]. Furthermore, oil spills in areas with warmer temperatures that have a high percentage of light hydrocarbons are likely to biodegrade unassisted [55].

The most important tradeoff is often the length of time that oil remains in the environment. In cases of low temperature and limited oxygen availability, unassisted degradation can result in very slow to negligible oil degradation [55]. This slow removal of the oil is a variable that should be weighed and considered before adopting this response.

4. Case Study – An analysis of the MV Rena oil spill

Having reviewed the individual responses and key questions involved in a spill response we consider how this knowledge could inform an active oil spill response. In a real oil spill situation, it is necessary to deal with evolving conditions and to consider the use of multiple responses at any given time. By looking at a complete spill from the beginning of the incident to the end of cleanup, it is possible to understand how decisions were made, and to see how the application of key questions and knowledge gained from previous research can inform a spill response in progress. We have examined the MV *Rena* oil spill in the Bay of

Plenty, New Zealand in October 2011 to highlight lessons from the response literature. This spill was chosen because it occurred recently and was well documented by Maritime New Zealand, allowing a detailed analysis of the spill conditions and response as they evolved over time.

4.1 Description of Situation [7]

The MV *Rena* was a cargo vessel that struck the Astrolabe Reef twelve nautical miles off the coast of New Zealand near Tauranga on October 5, 2011. The total volume of oil on board the ship was estimated at 1900 metric tons, the majority of which was bunker oil. Oil began leaking from the grounded vessel on the evening of October 5, and strong ocean currents pushed the oil in the direction of the shoreline. The weather was calm until the night of October 10, after which a storm system entered the area and oil started to wash up on nearby beaches. The spill occurred close to an important fish habitat and in the middle of the breeding season of native birds. On October 14, the hull of the ship cracked fully in two, speeding the release of oil and the intensification of cleanup operations on the beaches. In the next ten days the effort focused on the pumping of oil off the ship in order to prevent more oil being spilled. By end of October 2011, the situation was contained and the effort had mostly transitioned to cleanup operations of the oil and debris. Many beach restrictions were lifted on November 15, 2011, but in March 2012 small amounts of oil were still reported to be leaking. As of this writing, removal of the ship and assorted debris was still ongoing.

In their initial response to the MV *Rena* spill, Maritime New Zealand activated its Maritime Incident Response Team, whose aim was to refloat and remove the vessel from the reef without any release of fuel oil or hazardous cargo into the environment. This effort, along with ongoing efforts to pump oil from the damaged vessel when weather permitted, were very important to the cleanup. Preventing oil release

into the environment altogether precludes the need to remove it, and this was the primary focus of Maritime New Zealand's efforts.

In addition to preventing oil release, a number of corrective actions were taken to treat spilled oil. The dispersant Corexit 9500 was applied to the spill after 24 hours, and protective booms were eventually set up to guard many of the sensitive nearby beaches - the Tauranga Harbor and an area of extensive sheltered tidal flats (ESI index of 9A), salt marshes (10A) and mangroves (10D) [26] were threatened by the spill. Equipment to skim oil from the surface was also deployed, but it could not be used in the early days of the spill due to deterioration of weather conditions.

The size of the oil spill was continuously changing, and this, along with the movement of the oil slick, was well monitored, which allowed decisions about response strategy to be reevaluated on an ongoing basis. In later phases of the oil release, it was noted that the majority of the slick stayed in the area of the grounded vessel.

Like many oil spill cleanup operations, the initial response to this spill was hindered by delays in the decision-making process, which ultimately limited the available options. While Maritime New Zealand was quick to act when it became clear that the spill could not be contained, a pre-established plan of action would have assisted communication between the crew of the MV *Rena* and Maritime New Zealand and expedited the response [7]. As discussed above, cleanup of fresh oil is much easier than that of weathered oil, and substantial weathering occurs even in the first 24 hours after a spill.

4.2 Analysis of Response

Considering the spill from the perspective of the key questions reviewed in this paper can provide insight into how a practical summary of oil spill literature informs the response to an active oil

spill. The MV *Rena* spill was a continuous release of oil with a known maximum volume, and was a spill of hydraulic engine oil and bunker oil. Stopping the ongoing release was correctly a priority; the choice to use dispersants was however poorly informed because dispersants are largely ineffective on heavy oils, especially after weathering has occurred [118].

The spilled oil was predominantly on the surface of the water, especially during the initial release. Skimmer technology for bunker oil does exist, and the choice to deploy skimmers to clean up this surface spill was wise. This was unfortunately hampered by a combination of the aforementioned delays in the early response and poor weather. The deployment of containment booms was similarly restricted by timing and weather, but protective booms were somewhat effective in reducing oiling of the beaches.

Other responses that could have been considered are burning, fertilization, and non-intervention. Burning was likely precluded both by the presence of other vessels for removal of the oil from the *Rena*, and by the proximity to populated areas. Although detailed environmental baseline data for the area is not available, localized eutrophication events have occurred in the Tauranga basin [119], making fertilization a poor option. The excellent monitoring of oil movement and local currents showed strong currents would carry the spilled oil towards shore. This information made it clear that intervention was necessary.

While hindsight is the easiest lens through which to evaluate any oil spill response, there are several important lessons to be learned from the MV *Rena* spill. The first is that rapid decision-making improves the effectiveness of a response. While most of the decisions made by Maritime New Zealand were appropriate, having a decision-making framework in place for such an emergency would have expedited the response

process, allowing for faster deployment of containment booms and skimming equipment. The second is that environmental baseline data is essential. Knowledge of local eutrophication events prevented the costly and risky use of fertilizers in the Tauranga basin; having more detailed information could have helped determine if other areas of the spill could be fertilized. The third lesson is to understand the limitations of the technology available. The ineffectiveness of dispersant application to heavy, weathered oils is known [118], but it was used in this cleanup effort because that information was not communicated to decision makers. The following section outlines recommendations based on these lessons, including the gathering of baseline data, computer simulations, technological improvements to responses, and understanding of impacts.

5. Future Research Needs

All aspects of oil spill response can benefit from further research. These can be grouped into three major areas that tap different sets of technical expertise. Baseline environmental data should be collected at present and future drilling sites; this is a key immediate action that could spur research and inform the application of the responses discussed above. Computer modeling of the fate of released oil will assist in anticipating spill evolution when a spill occurs and benefit overall response implementation. Technical improvements to response technologies will improve efficacy of oil removal. Environmental impact studies for current and emerging technologies will assist in deciding when they are best applied to a spill.

5.1 Baseline Environmental Data

Collection of baseline data in an area that is at risk for an oil spill will help response planning by providing information about the resilient and fragile parts of an ecosystem. This data must be

collected before oil contamination occurs, and should incorporate local knowledge and priorities such as seasonal use of animal habitats [13, 120] or human activity [121, 122].

It is particularly important to collect baseline data that can inform and improve the application of response technologies. Detection of oil-degrading bacteria, as is possible with PhyloChip microarrays [123], and levels of limiting nutrients will help to predict whether significant hydrocarbon degradation could occur naturally. This data could inform potential application of fertilizers or sinking agents, and of the likelihood that oil left alone will naturally degrade in the environment. Knowledge of sensitive shoreline or underwater environments will smooth the process of prioritizing at-risk ecosystems for protection. Additionally, collection of baseline data about air quality [43] and other contaminant levels will help to evaluate whether an impacted environment has returned to pre-spill conditions, which will improve accountability for oil spill cleanup.

5.2 Computer Modeling

With sufficient baseline data about an area, it is possible to generate predictive models of the movement of oil in the environment. Oil evaporation has been modeled as a function of time or temperature, dependent on the initial oil composition [54]. Models of the release of oil from a reservoir [124], geographical distribution [71, 72, 125], and the mixing of oil with water in the absence of intervention [42, 59] are becoming increasingly common. More advanced models have also been generated that predict the rate at which oil will be removed from the environment using a particular response and use these inputs to calculate scenarios for cleanup [126]. This is invaluable in performing a cost-benefit analysis of a particular intervention and when considering the possibility of non-intervention as the most ecologically sound method for oil cleanup.

5.3 Technical Improvements

Improvements can be made to enhance skimming, burning and dispersant technologies. Absorbent materials with increased selectivity for hydrocarbons over water are needed to improve the overall removal efficiencies of skimmers. Their efficacy at removing heavier or partially emulsified oils also needs to be improved to broaden the utility of skimmers for a wider range of spills. A major drawback of all skimmer technology is its inability to effectively deal with debris; coarse filtration systems that protect oil-removing materials can ameliorate this [16]. Sorbent materials using natural waste products from local agriculture show promise as an alternative method of oil collection [73].

New burning agents that keep a fire burning continuously, cleanly, and work with a variety of oil types would improve burning efficiencies and reduce air pollution hazards. Ignition techniques, containment, and air quality monitoring could also be improved to ensure safe and effective *in situ* burning.

Dispersants are typically a treatment of last resort because of their potential to negatively affect organisms in the water column [34, 41, 92]. Use of currently existing dispersants would be improved by more comprehensive data about their effects in different environments, possibly through the use of species sensitive distributions [127]. New dispersants without components that are cytotoxic, teratogenic, or disruptive to the endocrine system of organisms in the marine environment could make dispersant application more viable. However, the repercussions of making oil itself more bioavailable are still of concern. Further improvements could include dispersants that degrade to non-toxic small molecules that supply limiting nutrients to microbial hydrocarbon degraders. Surfactants of bacterial origin, or that mimic bacterial biosurfactants, are a promising area of research

[128, 129]. Ideally, bio-based surfactants are biodegradable and enhance the activity of the whole hydrocarbon degrading microbial community [129, 130]. Advances in amino acid-based [131] and saccharide-based surfactants [132, 133] could also contribute significantly to the creation of less toxic dispersants.

Fertilization could be improved through studies optimizing quantities and types of fertilizers applied, and by understanding how to customize their application for each ecological scenario while considering entire oil-degrading microbial communities [130]. Additionally, coupling of fertilization with the use of dispersants as suggested above could assist degradation.

The treatment of weathered and emulsified oil remains one of the most significant technical challenges for addressing oil spills. Most technologies that work well on fresh oil, including burning, skimming, and dispersants, are largely ineffective on weathered oil. The same is generally true of bunker oil because its lack of volatile components makes the properties of bunker oil roughly approximate those of weathered crude. Although many spills of bunker oil are small, better methods to clean up this large fraction (48% by volume of all oil spilled in the marine environment) of spilled oil are necessary.

5.4 Environmental Impact of Responses

The extent to which immediate and long-term environmental impact is understood varies greatly between responses. In general these impacts are poorly studied, often because follow-up evaluation has not historically been considered part of the cleanup process [24]. In the case of physical removal technologies such as skimmers and booms, the main secondary impacts are site-specific habitat damage by human presence, but in chemically and biologically complex responses, the environmental impacts can be studied in a

broader sense.

In order to properly assess the risks and benefits of using dispersants, predictions of the effectiveness of the dispersant in producing the desired outcomes must be possible. These desired outcomes can be considered as opportunity costs of not using dispersants, such as avoidance of shoreline oiling or reducing the fire hazard to workers around the spill [134]. An understanding of how both oil and dispersants distribute in the environment and assessment of the effectiveness of dispersants in reducing shoreline oiling is crucial. Additionally, the risks of dispersant use in the particular ecosystem must be well characterized. Most data regarding dispersant effects on microbial degradation, for example, seem to indicate that dispersant introduction leads to slower oil degradation, but some indicate no change or even an increase in degradation rate [101]. Many other possible risks of dispersant use are also still not well understood, including sublethal effects of dispersants mixed with crude oil, effects of dispersants in deep water, movement and degradation of dispersants in the environment, and long-term environmental effects.

More research on dispersants is needed to fully inform decisions about their use. Better toxicity studies are needed, with careful consideration of relevant endpoints and organisms. This is especially true for dispersants that are not part of the Corexit family, since much of the data on modern dispersants was acquired using Corexit dispersants. It is also imperative to conduct appropriate environmental monitoring studies before, during and after dispersant application. While monitoring during cleanup is commonly done, baseline studies before a spill and long-term monitoring after a spill are much less common. This monitoring would also be improved by better analytical field methods. The only reliable method for detecting oil is GC-MS, which is difficult to do in the field [101]. The

traditional field method for oil detection is fluorometry, which is less reliable, although improvements are continually being made [135]. Relying on dispersant detection as a proxy for oil detection is also problematic, as the dispersants can persist after the oil has been degraded [41].

In areas where there is a tendency toward or a history of eutrophication events, it is particularly important to carefully consider the compounded effects of the application fertilizers. Although fertilizers have been extensively used as a response, it is important to continue to fine-tune their content and ratios so as to best harness the degradation capacity of the natural hydrocarbon-degrading microbial communities. A database of baseline data of the affected area, as well as thorough understanding of the ecosystems affected by the spill will greatly aid in evaluating the risks and benefits of the application of fertilizers.

A response that is currently not legal in most countries because of its historic negative impacts is the use of sinking agents; as a result, little is known about the technique [16]. While extreme caution in the application of sinking agents in coastal areas is still warranted, the movement of underwater drilling to locations further offshore, where the ocean is much deeper and the biota on the sea floor are less dense, suggests that this technique should be revisited. Studying the extent and effects of leaching on the ocean floor would help determine the appropriate uses of sinking agents. The extent and effects of leaching on the ocean floor and more thorough surveys of deep-water organisms would inform the potential safe use of sinking agents.

With increased collection of background data, it becomes possible to quantify the impact of not intervening on the recovery of an ecosystem. Further research is needed to elucidate when and where the choice to not intervene is appropriate. The ecology and *in situ* physiology

of natural marine hydrocarbon-degrading microbial communities requires further study, as does the determination of conditions where unassisted biodegradation is effective. Studying the environments and cases where intervention has resulted in an added stress to the system will give scientific weight to non-intervention as a reasonable response.

6. Conclusions

There is a growing voice in the oil spill literature [5, 9, 42, 44, 58] calling for decision-making tools that encompass the complexity of environmental problem solving. This review provides a framework to assist in the communication of this complexity to diverse stakeholders. This takes the form of a series of decision points based on the nature of oil spilled and the environment in which a spill takes place.

Underlying these guiding questions is a strong emphasis on ecological awareness. This context contributes to the execution of an environmental management strategy that ensures rapid recovery and the maintenance of ecosystem resilience and biodiversity. This in turn requires that ecological baseline data be collected in locations where oil spills are likely.

In addition to the need for ecological data, this review identifies opportunities for improving existing oil spill responses through technological advances and computer modeling. These measures will improve oil spill response capacity and should particularly be considered in new oil drilling regions. Effective and transparent response strategies will help stakeholders preserve the ability of the ecosystem to recover from oil spills and retain function in the face of anthropological stresses.

Acknowledgements The authors are grateful for the assistance of J. Kulp and for the guidance of J. Arnold, J. Guth, A. Kokai, A. Iles, C. Rosen, M. Schwarzman and M. Wilson. Special thanks go to

M. Schwarzman and A. Iles for manuscript assistance. The authors would also like to thank T. Ryerson for access to oil composition data.

References

1. *International Energy Outlook*, 2010, U.S. Energy Information Administration Office of Integrated Analysis and Forecasting.
2. Reichman, O.J., M.B. Jones, and M.P. Schildhauer, *Challenges and Opportunities of Open Data in Ecology*. *Science*, 2011. **331**(6018): p. 703-705.
3. Thiffeault, J.L., *Chaos in the Gulf*. *Science*, 2010. **330**(6003): p. 458-459.
4. Stokstad, E., *GULF OIL DISASTER Looking Beyond the Spill, Obama Highlights Long-Term Restoration*. *Science*, 2010. **328**(5986): p. 1618-1619.
5. Safford, T.G., J.D. Ulrich, and L.C. Hamilton, *Public perceptions of the response to the Deepwater Horizon oil spill: Personal experiences, information sources, and social context*. *J Environ Manage*, 2012. **113**: p. 31-39.
6. *Oil Spill Case Histories 1967-1991 Summaries of Significant U.S. and International Spills*, 1992, National Oceanic and Atmospheric Administration: Seattle, Washington.
7. Maritime New Zealand. *Maritime New Zealand's 2011 media releases*. 2011 [cited Access December 13, 2011]; Available from: <http://www.maritimenz.govt.nz/News/Media-releases-2011/Media-releases-2011.asp>.
8. Crone, T.J. and M. Tolstoy, *Magnitude of the 2010 Gulf of Mexico Oil Leak*. *Science*, 2010. **330**(6004): p. 634-634.
9. Boesch, D., *Deep-water drilling remains a risky business*. *Nature*, 2012. **484**(7394): p. 289.
10. Watson, T. *In Kulluk's Wake, Deeper Debate Roils on Arctic Drilling*. 2013 [cited Access January 28, 2013]; Available from: <http://news.nationalgeographic.com/news/2013/130112-in-kulluks-wake-deeper->

- [debate-roils-on-arctic-drilling/](#).
11. Jones, H.P. and O.J. Schmitz, *Rapid Recovery of Damaged Ecosystems*. PLoS ONE, 2009. **4**(5): p. e5653.
 12. Dubansky, B., et al., *Multitissue Molecular, Genomic, and Developmental Effects of the Deepwater Horizon Oil Spill on Resident Gulf Killifish (*Fundulus grandis*)*. Environ. Sci. Technol., 2013. **47**(10): p. 5074-5082.
 13. Kennedy, C.J. and S.-M. Cheong, *Lost ecosystem services as a measure of oil spill damages: A conceptual analysis of the importance of baselines*. J Environ Manage, 2013. **128**: p. 43-51.
 14. Laws, E.A., *Aquatic Pollution: An Introductory Text*. 3rd ed 2000, New York: John Wiley and Sons.
 15. U.S. EPA. *Response to Oil Spills*. 2011 [cited Access September 7, 2011]; Available from: <http://www.epa.gov/emergencies/content/learning/response.htm>.
 16. Fingas, M., *The Basics of Oil Spill Cleanup*. 2nd ed, ed. J. Charles 2001, Boca Raton, FL: CRC Press LLC.
 17. Walker, A.H., et al., *Selection Guide for Oil Spill Applied Technologies. Volume I - Decision Making*, 2003, Scientific and Environmental Associates, Inc.: Cape Charles, VA.
 18. Committee on Oil in the Sea, Ocean Studies Board and Marine Board, Divisions of Earth and Life Studies and Transportation Research Board, National Research Council, *Oil in the Sea III: Inputs, Fates, and Effects* 2003, Washington, DC: The National Academies Press.
 19. McNutt, M.K., et al., *Applications of science and engineering to quantify and control the Deepwater Horizon oil spill*. PNAS, 2012. **109**(50): p. 20222-20228.
 20. Machlis, G.E. and M.K. McNutt, *Scenario-Building for the Deepwater Horizon Oil Spill*. Science, 2010. **329**(5995): p. 1018-1019.
 21. Munilla, I., et al., *Mass mortality of seabirds in the aftermath of the Prestige oil spill*. Ecosphere, 2011. **2**(7): p. art83.
 22. Paine, R.T., et al., *Trouble on Oiled Waters: Lessons from the Exxon Valdez Oil Spill*. Annu. Rev. Ecol. Sys., 1996. **27**(1): p. 197-235.
 23. Folke, C., et al., *Regime shifts, resilience, and biodiversity in ecosystem management*. Annu. Rev. Ecol. Evol. Syst., 2004. **35**: p. 557-581.
 24. Vandermeulen, J.H. and C.W. Ross, *Oil Spill Response in Freshwater: Assessment of the Impact of Cleanup as a Management Tool*. J. Environ Manage, 1995. **44**: p. 297-308.
 25. Walker, B., et al., *Resilience, adaptability and transformability in social-ecological systems*. Ecology and Society, 2004. **9**(2): p. art5.
 26. NOAA, *Environmental Sensitivity Index Guidelines, NOAA Technical Memorandum NOS OR&R 11*, 2002, NOAA Office of Response and Restoration: Seattle, Washington.
 27. Shigenaka, G., et al., *Oil Spills in Coral Reefs, Planning and Response Consideration, 2nd Edition*, 2010, NOAA: Office of Response and Restoration.
 28. Hoff, R., et al., *Oil Spills in Mangroves, Planning and Response Considerations*, H. R., Editor 2002, NOAA, Ocean Service, Office of Response and Restoration.
 29. SINTEF. *SINTEF OSCAR: Oil Spill Contingency and Response 2009* [cited Access October 31, 2009]; Available from: <http://www.sintef.no>.
 30. Dewling, R.T. and L.T. McCarthy, *Chemical Treatment of Oil Spills*. Environ. Int., 1980. **3**(2): p. 155-162.
 31. Graham, P., *Deep Sea Oil Spill Cleanup Techniques: Applicability, Trade-offs and Advantages*, in *Discovery Guides* 2010, ProQuest. p. 1-15.
 32. Li, Z., et al., *Effects of temperature and wave conditions on chemical dispersion*

- efficacy of heavy fuel oil in an experimental flow-through wave tank. Mar. Pollut. Bull., 2010. 60(6): p. 1550-1559.*
33. Li, Z., et al., *Evaluating crude oil chemical dispersion efficacy in a flow-through wave tank under regular non-breaking wave and breaking wave conditions. Marine Pollution Bulletin, 2009. 58(5): p. 735-44.*
 34. Milinkovitch, T., et al., *Liver antioxidant and plasma immune responses in juvenile golden grey mullet (Liza aurata) exposed to dispersed crude oil. Aquat. Toxicol., 2011. 101(1): p. 155-164.*
 35. Oudot, J., F.X. Merlin, and P. Pinvidic, *Weathering Rates of Oil Components in a Bioremediation Experiment in Estuarine Sediments. Mar. Environ. Res., 1998. 45(2): p. 113-125.*
 36. Ramachandran, S.D., et al., *Influence of salinity and fish species on PAH uptake from dispersed crude oil. Marine Pollution Bulletin, 2006. 52(10): p. 1182-9.*
 37. Swannell, R.P., K.L. Lee, and M. McDonagh, *Field Evaluations of Marine Oil Spill Bioremediation. Microbiol. Rev., 1996. 60(2): p. 342-365.*
 38. Venosa, A.D. and E.L. Holder, *Biodegradability of dispersed crude oil at two different temperatures. Marine Pollution Bulletin, 2007. 54(5): p. 545-53.*
 39. Atlas, R. and T. Hazen, *Oil biodegradation and bioremediation: A tale of the two worst spills in US history. Environ. Sci. Technol., 2011. 45(16): p. 6709-6715.*
 40. Kessler, J., et al., *A persistent oxygen anomaly reveals the fate of spilled methane in the deep Gulf of Mexico. Science, 2011. 331(6015): p. 312-315.*
 41. Kujawinski, E.B., et al., *Fate of Dispersants Associated with the Deepwater Horizon Oil Spill. Environmental science & technology, 2011. 45: p. 1298-1306.*
 42. Peterson, C.H., et al., *A Tale of Two Spills: Novel Science and Policy Implications of an Emerging New Oil Spill Model. BioScience, 2012. 62(5): p. 461-469.*
 43. Ryerson, T.B., et al., *Atmospheric emissions from the Deepwater Horizon spill constrain air-water partitioning, hydrocarbon fate, and leak rate. Geophys. Res. Lett., 2011. 38: p. L07803.*
 44. Carriger, J.F. and M.G. Barron, *Minimizing Risks from Spilled Oil to Ecosystem Services Using Influence Diagrams: The Deepwater Horizon Spill Response. Environ. Sci. Technol., 2011. 45(18): p. 7631-7639.*
 45. Oil Eater Brand. *Oil Eater Brand Absorbent Products. 2006 2006 [cited Access November 29, 2006]; Available from: <http://www.oileater.com/SpillKits.html>.*
 46. Etkin, D.S., *Analysis of past marine oil spill rates and trends for future contingency planning. Proc. 25th Arctic & Marine Oilspill Program Tech. Sem., 2002: p. 227-252.*
 47. Nuka Research & Planning Group LLC and Cape International Inc, *Vessel Traffic in the Aleutians Subarea, 2006, Alaska Department of Environmental Conservation.*
 48. Etkin, D.S., *Analysis of Oil Spill Trends US and Worldwide. Proc 2001 Int. Oil Spill Conf., 2001: p. 1291-1300.*
 49. McNutt, M.K., et al., *Review of flow rate estimates of the Deepwater Horizon oil spill. PNAS, 2012. 109(50): p. 20260-20267.*
 50. Cappiello, D. *New BP challenge to spill size could affect fine. 2010 [cited Access June 4, 2010]; Available from: <http://www.apnewsarchive.com/2010/New-BP-challenge-to-spill-size-could-affect-fine/id-a0247f07d96e48239ed148314b7c6d7e>.*
 51. Wolska, L., et al., *Sources and Fate of PAHs and PCBs in the Marine Environment. Crit. Rev. Env. Sci. Tech., 2012. 42: p. 1172-1189.*
 52. Connell, D.W. and G.J. Miller, *Petroleum hydrocarbons in aquatic ecosystems - Behavior and effects of sublethal concentrations: Part I. Crit. Rev. Env. Contr.,*

1980. **11**(1): p. 37-104.
53. NOAA. *Incident News M/V Cosco Busan*. 2007 [cited Access January 24, 2007]; Available from: <http://www.incidentnews.gov/incident/7708>.
 54. Wang, Z., et al., *Characteristics of Spilled Oils, Fuels, and Petroleum Products: 1. Composition and Properties of Selected Oils*, 2003.
 55. American Academy of Microbiology, *Microbes & Oil Spills FAQ*, 2011, American Academy of Microbiology: Washington, DC.
 56. Tully, P.R., *Removal of floating oil slicks by the controlled combustion technique.*, in *Oil on the Sea*, D.P. Hoult, Editor 1969, Plenum Press: New York. p. 81-91.
 57. Johansen, Ø., et al., *Deep Spill JIP-Experimental Discharges of Gass and Oil at Helland Hansen*, 2000: Norway.
 58. Reible, D., *After the oil is no longer leaking...* Environ. Sci. Technol., 2010. **44**(15): p. 5685-5686.
 59. Mezic, I., et al., *A New Mixing Diagnostic and Gulf Oil Spill Movement*. Science, 2010. **330**(6003): p. 486-489.
 60. Masutani, S.M. and E.E. Adams, *Experimental Study of Multi-Phase Plumes with Applications to Deep Ocean Spills*, 2001, Hawai'i Natural Energy Institute.: Honolulu, HI.
 61. Jensen, J.R., et al., *Environmental sensitivity index (ESI) mapping for oil spills using remote sensing and geographic information system technology*. Int. J. Geogr. Inf. Sci., 1990. **4**(2): p. 181-201.
 62. Jensen, J.R., J.N. Halls, and J. Michel, *Approach to Environmental Sensitivity Index (ESI) Mapping for Oil Contingency Planning and Response*. Photogramm. Eng. Rem. S., 1998. **64**(10): p. 1003-1014.
 63. Jensen, J.R., et al., *Coastal environmental sensitivity mapping for oil spills in the United Arab Emirates using remote sensing and GIS technology*. Geocarto Int., 1993. **8**(2): p. 5-13.
 64. Populus, J., et al., *An assessment of environmental sensitivity to marine pollutions: solutions with remote sensing and Geographical Information Systems (GIS)*. Int. J. Remote Sens., 1995. **16**(1): p. 3-15.
 65. Mendoza-Cantú, A., et al., *Identification of environmentally vulnerable areas with priority for prevention and management of pipeline crude oil spills*. J. Environ Manage, 2011. **92**: p. 1706-1713.
 66. Halber, D. *New Solar Cell, Oil Spill Remediation Technologies Unveiled*. [HTML File] 2010 [cited Access April 1, 2010]; Available from: <http://web.mit.edu/mitei/news/spotlights/remediation-tech.html>.
 67. LaMonica, M. *MITs New Paper Chase: Cheap Solar Cells*. [HTML File] 2010 [cited Access April 1, 2010]; Available from: http://news.cnet.com/8301-11128_3-20019885-54.html.
 68. Westermeyer, W.E., *Oil spill response capabilities in the United States*. Environ. Sci. Tech., 1991. **25**(2): p. 196-200.
 69. National Academy of Science, *Petroleum in the Marine Environment* 1975, Washington, DC: National Academy of Sciences.
 70. NOAA. *Exxon Valdez Oil Spill: Responding to the Spill*. 2012 July 19, 2012 [cited Access November 30, 2012]; Available from: <http://celebrating200years.noaa.gov/event/exxonvaldez/welcome.html - responding>.
 71. Abascal, A.J., et al., *Analysis of the Reliability of a Statistical Oil Spill Response Model*. Mar. Pollut. Bull., 2010. **60**: p. 2099-2110.
 72. Murray, S., *Turbulent Diffusion of Oil in the Ocean*. Limnol. Oceanogr., 1972. **XVII**(5): p. 651-660.
 73. Al-Majed, A.A., A.R. Adebayo, and M.E. Hossain, *A sustainable approach to controlling oil spills*. J. Environ Manage,

2012. **113**: p. 213-227.
74. International Tanker Owners Pollution Federation. *Alternative Techniques*. 2010 [cited Access April 1, 2010]; Available from: <http://www.itopf.com/spill-response/clean-up-and-response/alternative-techniques/>.
 75. U.S. OTA, *Coping With an Oiled Sea: An Analysis of Oil Spill Response Technologies*, 1990, U.S. Congress Office of Technology Assessment: Washington, DC. p. 1-74.
 76. U.S. EPA. *Exxon Valdez*. 2011 [cited Access November 15, 2011]; Available from: <http://www.epa.gov/osweroe1/content/learning/exxon.htm>.
 77. Florida DEP, *Deepwater Horizon Oil Spill Response Treatment, Reuse and Disposal Options*, 2010, Florida Department of Environmental Protection: Tallahassee, Florida. p. 1-43.
 78. Deepwater Horizon JIC. *The Ongoing Administration-Wide Response to the Deepwater BP Oil Spill*. 2010 September 17, 2010 [cited Access January 15, 2010]; Available from: <http://www.restorethegulf.gov/release/2010/09/17/ongoing-administration-wide-response-deepwater-bp-oil-spill>.
 79. Bech, C., P. Sveum, and I. Buist, *In-situ burning of emulsions: the effects of varying water content and degree of evaporation*. Proc. 15th Arctic and Marine Oilspill Program (AMOP) Technical Seminar, 1992: p. 547-559.
 80. Fingas, M.F., et al. *The Newfoundland Offshore Burn Experiment- NOBE*. in *In Situ Burning Oil Spill Workshop*. 1994. Lake Buena Vista, FL: NIST.
 81. Special Monitoring of Applied Response Technologies, *SMART at the New Carissa Oil Spill*, NOAA, Editor 2006, U.S. Department of Commerce, NOAA's National Ocean Service, Office of Response and Restoration.
 82. Michel, J., et al., *In-situ Burning, A Decision-maker's Guide to In-situ Burning*, 2005, Regulatory Analysis and Scientific Affairs, American Petroleum Institute.
 83. U.S. EPA. *Questions and Answers on Dispersants*. 2011 October 14, 2011 [cited Access October 19, 2011]; Available from: <http://www.epa.gov/bpspill/dispersants-ganda.html>.
 84. U.S. EPA. *Threats from Oil Spills*. 2011 [cited Access January 25, 2011]; Available from: <http://www.epa.gov/emergencies/content/learning/effects.htm>.
 85. Chandrasekar, S., G.a. Sorial, and J.W. Weaver, *Dispersant Effectiveness on Three Oils Under Various Simulated Environmental Conditions*. Environmental Engineering Science, 2005. **22**(3): p. 324-336.
 86. Nordvik, A.B., *The Technology Windows-of-Opportunity for Marine Oil Spill Response as Related to Oil Weathering and Operations*. Spill Science & Technology Bulletin, 1995. **2**(1): p. 17-46.
 87. U.S. EPA. *Alphabetical List of NCP Product Schedule Products with Links to Technical Product Summaries*. 2013 [cited Access May 3, 2013]; Available from: http://www.epa.gov/osweroe1/content/ncp/product_schedule.htm.
 88. Nelson-Smith, A., *Oil Pollution and Marine Ecology* 1972, London: Elek.
 89. Nelson-Smith, A., *Oil emulsifiers and marine life*. The Journal of the Devon Trust for Nation Conservation, Ltd. Supplement. Conservation and the Torrey Canyon, 1967(July): p. 29-33.
 90. Wilson, K., *Toxicity of Oil-Spill Dispersants to Embryos and Larvae of Some Marine Fish*, in *Marine Pollution and Sea Life*, M. Ruivo, Editor 1970, Fishing News Ltd: London. p. 318-322.
 91. Kühnhold, W., *The Influence of Crude Oils on Fish Fry*, in *Marine Pollution and Sea Life*, M. Ruivo, Editor 1970, Fishing News Ltd: London. p. 315-318.
 92. Lindén, O., *The Influence of Crude Oil and Mixtures of Crude Oil/Dispersants on the*

- Ontogenic Development of the Baltic Herring, Clupea harengus membras L.* *Ambio*, 1976. **5**(3): p. 136-140.
93. Slade, G.J., *Effect of Ixtoc I Crude Oil and Corexit 9527 Dispersant on Spot (Leiostomus xanthurus) Egg Mortality.* *Bull. Environm. Contam. Toxicol.* , 1982. **29**: p. 525-530.
 94. Khan, A., *Oil dispersant effects remain a mystery*, in *Los Angeles Times* 2010.
 95. Judson, R.S., et al., *Analysis of Eight Oil Spill Dispersants Using Rapid, In Vitro Tests for Endocrine and Other Biological Activity.* *Environmental science & technology*, 2010. **44**(15): p. 5979-85.
 96. Barron, M.G., *Ecological Impacts of the Deepwater Horizon Oil Spill: Implications for Immunotoxicity.* *Toxicol Pathol*, 2012. **40**: p. 315-320.
 97. Calabrese, E.J., *Paradigm lost, paradigm found: The re-emergence of hormesis as a fundamental dose response model in the toxicological sciences.* *Environ. Pollut.*, 2005. **138**(3): p. 378-411.
 98. Lutz, W.K., *Dose–response relationships in chemical carcinogenesis: superposition of different mechanisms of action, resulting in linear–nonlinear curves, practical thresholds, J-shapes.* *Mutat. Res.*, 1998. **405**(2): p. 117-124.
 99. Coe, H., *Aerosol Chemistry and the Deepwater Horizon Spill.* *Science*, 2011. **331**(6022): p. 1273-1274.
 100. de Gouw, J.A., et al., *Organic Aerosol Formation Downwind from the Deepwater Horizon Oil Spill.* *Science*, 2011. **331**(6022): p. 1295-1299.
 101. Fingas, M., *A Review of Literature Related to Oil Spill Dispersants, 1997-2008*, 2008, Spill Science: Edmonton, AB.
 102. Chandrasekar, S., G. Sorial, and J. Weaver, *Dispersant effectiveness on oil spills – impact of salinity.* *ICES Journal of Marine Science*, 2006. **63**(8): p. 1418-1430.
 103. Lunel, T., et al. *The Net Environmental Benefit of a Successful Dispersant Operation at the Sea Empress Incident.* in *International Oil Spill Conference.* 1997.
 104. Jernelöv, A. and O. Lindén, *Ixtoc I: A Case Study of the World’s Largest Oil Spill.* *Ambio*, 1981. **10**(6): p. 299-306.
 105. Sigma Aldrich Corporation, Product Safety – Americas Region, *Calcium Carbonate; MSDS No. Y7512352009*, St. Louis, MO.
 106. Weelink, S.A.B., M.H.A. van Eekert, and A.J.M. Stams, *Degradation of BTEX by anaerobic bacteria: physiology and application.* *Rev. Environ. Sci. Biotechnol.*, 2010. **9**(4): p. 359-385.
 107. Blumer, M., et al., *A small oil spill.* *Environment*, 1971. **13**(2): p. 2-12.
 108. McKew, B., et al., *Efficacy of intervention strategies for bioremediation of crude oil in marine systems and effects on indigenous hydrocarbonoclastic bacteria.* *Environ. Microbiol.*, 2007. **9**(6): p. 1562-1571.
 109. Hazen, T.C., et al., *Deep-sea oil plume enriches indigenous oil-degrading bacteria.* *Science*, 2010. **330**(6001): p. 204-208.
 110. U.S. OTA, *Biotechnology for Marine Oil Spills* 1991, Congress of the United States Office of Technology Assessment: Washington, DC.
 111. Head, I.M., D.M. Jones, and W.F.M. Röling, *Marine microorganisms make a meal of oil.* *Nature Reviews Microbiology*, 2006. **4**(3): p. 173-182.
 112. Röling, W.F., et al., *Robust hydrocarbon degradation and dynamics of bacterial communities during nutrient-enhanced oil spill bioremediation.* *Appl. Environ. Microbiol.*, 2002. **68**(11): p. 5537–5548.
 113. Röling, W.F., et al., *Bacterial community dynamics and hydrocarbon degradation during a field-scale evaluation of bioremediation on a mudflat beach contaminated with buried oil.* *Appl. Environ. Microbiol.* , 2004. **70**(5): p. 2603–2613.
 114. Jiménez, N., et al., *The Prestige oil spill. 2. Enhanced biodegradation of a heavy fuel oil*

- by the use of an Oleophilic Fertilizer under field conditions *Environ. Sci. Technol.*, 2006. **40**(8): p. 2578-2585.
115. Wang, Z., et al., *Comparison of oil composition changes due to biodegradation and physical weathering in different oils*. *J Chromatogr, A*, 1998. **809**(1-2): p. 89-107.
 116. Radovic, J.R., et al., *Post-incident monitoring to evaluate environmental damage from shipping incidents: Chemical and biological assessments*. *J. Environ Manage*, 2012. **109**: p. 136-153.
 117. Efrogmson, R.A., J.P. Nicolette, and G.W. Suter II, *A Framework for Net Environmental Benefit Analysis for Remediation or Restoration of Petroleum-Contaminated Sites*, 2003, ORNL Environmental Sciences Division: Oak Ridge, Tennessee.
 118. Scholz, D.K., et al., *A Decision-Maker's Guide to Dispersants: A Review of the Theory and Operational Requirements*, 1998, American Petroleum Institute: Cape Charles, VA.
 119. Cromarty, P. and D.A. Scott, *A directory of wetlands in New Zealand*, 2003, Department of Conservation: Wellington, NZ. p. 1-46.
 120. Burke, C.M., W.A. Montevecchi, and F.K. Wiese, *Inadequate environmental monitoring around offshore oil and gas platforms on the Grand Bank of Eastern Canada: Are risks to marine birds known?* *J. Environ Manage*, 2012. **104**: p. 121-126.
 121. Castanedo, S., et al., *Oil spill vulnerability assessment integrating physical, biological and socio-economical aspects: Application to the Cantabrian coast (Bay of Biscay, Spain)*. *J. Environ Manage*, 2009. **91**: p. 149-159.
 122. de Andrade, M.M.N., et al., *A socioeconomic and natural vulnerability index for oil spills in an Amazonian harbor: A case study using GIS and remote sensing*. *J. Environ Manage*, 2010. **91**: p. 1972-1980.
 123. DeSantis, T.Z., Brodie, E.L., Moberg, J.P., Zubieta, I.X., Piceno, Y.M., Andersen, G.L., *High-density Universal 16S rRNA Microarray Analysis Reveals Broader Diversity Than Typical Clone Library When Sampling the Environment*. *Microb. Ecol.*, 2007. **53**: p. 371-83.
 124. Hsieh, P.A., *Computer Simulation of Reservoir Depletion and Oil Flow from the Macondo Well Following the Deepwater Horizon Blowout*, 2010, U.S. Department of the Interior, U.S. Geological Survey: Reston, VA.
 125. El-Fadel, M., R. Abdallah, and G. Rachid, *A modeling approach toward oil spill management along the Eastern Mediterranean*. *J. Environ Manage*, 2012. **113**: p. 93-102.
 126. Zhong, Z. and F. You, *Oil spill response planning with consideration of physicochemical evolution of the oil slick: A multiobjective optimization approach*. *Comput. Chem. Eng.*, 2011. **35**(8): p. 1614-1630.
 127. Barron, M.G., M.J. Hemmer, and C.R. Jackson, *Development of aquatic toxicity benchmarks for oil products using species sensitivity distributions*. *Integr Environ Assess Manag*, 2013. doi 10.1002/ieam.1420.
 128. Ron, E.Z. and E. Rosenberg, *Biosurfactants and oil bioremediation*. *Curr. Opin. Biotechnol.*, 2002. **13**(3): p. 249-252.
 129. Cameotra, S.S. and J.-M. Bollag, *Biosurfactant-Enhanced Bioremediation of Polycyclic Aromatic Hydrocarbons*. *Crit. Rev. Env. Sci. Tech.*, 2003. **33**(2): p. 111-126.
 130. McGenity, T.J., et al., *Marine crude-oil biodegradation: a central role for interspecies interactions*. *Aquat. Biosyst.*, 2012. **8**(1): p. 10.
 131. Morán, M.C., et al., *"Green" amino acid-based surfactants*. *Green Chem.*, 2004. **6**(5): p. 233-240.
 132. Queneau, Y., et al., *Recent progress in the synthesis of carbohydrate-based amphiphilic materials: the examples of*

- sucrose and isomaltulose*. Carbohydr. Res., 2008. **343**(12): p. 1999-2009.
133. Venkataraman, P., et al., *Attachment of a Hydrophobically Modified Biopolymer at the Oil–Water Interface in the Treatment of Oil Spills*. ACS Appl. Mater. Interfaces, 2013. **5**(9): p. 3572-3580.
134. Coelho, G., J. Clark, and D. Aurand, *Toxicity testing of dispersed oil requires adherence to standardized protocols to assess potential real world effects*. Environ. Pollut., 2013. **177**: p. 185-188.
135. Mendoza, W.G., D.D. Riemer, and R.G. Zika, *Application of fluorescence and PARAFAC to assess vertical distribution of subsurface hydrocarbons and dispersant during the Deepwater Horizon oil spill*. Environ. Sci.: Processes Impacts, 2013. **15**: p. 1017-1030.