

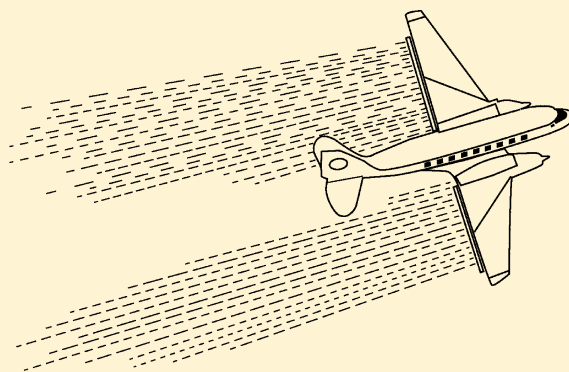


Oil Spill Dispersants: Boon or Bane?

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ABSTRACT: Dispersants provide a reliable large-scale response to catastrophic oil spills that can be used when the preferable option of recapturing the oil cannot be achieved. By allowing even mild wave action to disperse floating oil into tiny droplets ($<70\ \mu\text{m}$) in the water column, seabirds, reptiles, and mammals are protected from lethal oiling at the surface, and microbial biodegradation is dramatically increased. Recent work has clarified how dramatic this increase is likely to be: beached oil has an environmental residence of years, whereas dispersed oil has a half-life of weeks. Oil spill response operations endorse the concept of net environmental benefit, that any environmental costs imposed by a response technique must be outweighed by the likely benefits. This critical review discusses the potential environmental debits and credits from dispersant use and concludes that, in most cases, the potential environmental costs of adding these chemicals to a polluted area are likely outweighed by the much shorter residence time, and hence integrated environmental impact, of the spilled oil in the environment.



INTRODUCTION

Oil fuels our modern world, accounting for some 33% of energy consumption in 2013; daily consumption was 87 million barrels per day.¹ Some of this crude oil is produced from wells drilled under the sea, and a large percentage travels by sea between production and consumption. Despite the best efforts of the oil and shipping industries, some gets spilled. Catastrophic spills appropriately garner the public's attention, although, in fact, most spills are rather small. Natural seeps are likely the largest contributor of oil to the world's oceans, followed by nonpoint sources on land.² Tanker accidents are becoming less common,³ but it is still true that a few large spills contribute the most oil released to the sea by ships, and where such spills occur, they release far more oil in a few days than even the most active seeps. The tragic 2010 blowout from the *Deepwater Horizon* well⁴ is a reminder that large releases can also occur from drilling operations.

Crude oil has been part of the biosphere for millions of years,⁵ and a large number of microbes, both prokaryotic⁶ and eukaryotic,⁷ have evolved to consume it. Biodegradation is the eventual fate for all spilled oil that is not collected or burned, and both collection and combustion require that spilled oil be corralled with booms.⁸ While skimming can be an effective process if equipment is close to hand and the weather is reasonably calm, and is frequently part of oil spill response plans (e.g., refs 9–12), large spills in remote areas can spread so quickly that skimming becomes extremely difficult. For example, the *Deepwater Horizon* response, despite enormous efforts, collected only some 3% of the oil released and burned another 5%.⁴ Considerable research has been expended, therefore, on trying to enhance the rate of oil biodegradation.

Oil is an unusual substrate for microbial growth for two distinct reasons. On the one hand, most oil molecules have low density and are very sparingly soluble, so oil tends to stay as surface slicks or droplets dispersed by wave action. Biodegradation is then limited by the surface area of the oil–water interface. On the other, whereas hydrocarbons are rich sources of carbon and energy, oil contains no other useful elements for microbial growth. Nitrogen and phosphorus are the most usual limiting nutrients in the sea,¹³ followed by iron and other trace requirements.¹⁴ While seawater contains trace levels of these nutrients,¹⁵ the biodegradation of significant concentrations of oil, such as on a shoreline, is likely to exhaust the local supply. Bioremediation, the stimulation of biodegradation, thus aims to overcome these two limitations.

In the case of oil stranded on shorelines in Prince William Sound AK following the spill from the *Exxon Valdez*, the first response was to remove oil from beaches by washing it back to the sea and collecting it with skimmers.¹⁶ This had the effect of leaving a relatively thin film of oil on the gravel and rocks of the intertidal (and sometimes supra-tidal) zone, and this was bioremediated by the careful addition of oleophilic and slow-release fertilizers to increase the supply of bioavailable nitrogen and phosphorus. This worked quite well, stimulating oil biodegradation between 2- and 5-fold without causing any additional adverse effects,^{17–20} but it should be born in mind that the oil had already been on the shoreline for a year before the quantitative experiments reported therein were begun.

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Floating oil presents different challenges. Floating oil is a very real hazard to diving birds and mammals (e.g., refs 21 and 22), and oil that beaches is a hazard to shorebirds,²³ invertebrates,^{24,25} and mangroves.²⁶ Ameliorating these hazards was a primary impetus for the initial development of oil spill dispersants in the 1970s.²⁷ Modern dispersants are complex mixtures of anionic and neutral surfactants in a hydrocarbon solvent (e.g., ref 28) that lower the interfacial tension between oil and water so that minimal wave action and turbulence can disperse the oil into tiny droplets ($<70\ \mu\text{m}$) in the water column. Such droplets are essentially neutrally buoyant, so with minimal turbulence they stay in the water column and diffuse apart. Concentrations of dispersed oil may be ≈ 1000 ppm in the first minutes after dispersion, but they fall to a few ppm, in a correspondingly larger volume, within hours, and to sub parts per million levels within a day.^{29–34} Furthermore, even these concentrations are found only in the top few meters of the sea. Similarly, dispersants can harness the ejection turbulence of oil emanating from an uncontrolled subsea release and allow the formation of tiny oil droplets in the deep sea;^{4,34–37} again, the droplets diffuse apart until they are in the sub parts per million concentration range. This diffusive dilution means that, although the levels of nutrients in the sea are relatively low,¹³ it does not take long for oil concentrations to fall so that even those low levels are adequate for significant and rapid biodegradation. Hazen et al.^{14,35} measured half-lives of *n*-alkanes of a few days in the dilute ($2\text{--}442\ \text{ppb}^{34}$) dispersed submarine plume from the *Deepwater Horizon* at $1100\text{--}1220\ \text{m}$ (and $5\ ^\circ\text{C}$), and very similar results were reported for a broad array of individual hydrocarbons at low concentrations in New Jersey seawater at $8\ ^\circ\text{C}$,^{36,37} in a flume in Trondheim, Norway,³⁸ at $30\text{--}32\ ^\circ\text{C}$ and in water off the Penang, Malaysia, shore³⁹ at $27.5\ ^\circ\text{C}$. The approximate biodegradation half-life of the total measurable hydrocarbons was $11\text{--}14$ days, both at low oil concentrations with indigenous nutrients^{36,38} (2.5 and 43 ppm oil, respectively) and at slightly higher concentrations (100 ppm oil) with added nutrients.³⁹ Even the four ring aromatic chrysene and its methyl-, dimethyl-, and ethyl-alkylated forms had half-lives on the order of a month.³⁶

■ DISPERSANTS

Dispersants have been used on a large scale in many responses, notably, the 1993 *Braer* wreck in the Shetland Islands,⁴⁰ the 1996 *Sea Empress* spill in South Wales,⁴¹ and the 2010 *Deepwater Horizon* blowout in the Gulf of Mexico.³³ Seven spills in the US portion of the Gulf of Mexico were treated with dispersants between 1995 and 2004.⁴² Dispersants are stockpiled, with equipment for their use, in large quantities around the world,⁴³ and substantial illustrated guidelines for their use are freely available.⁴⁴ Nevertheless, their deployment is still controversial, for clearly dispersants are not without potential drawbacks. Most dispersants are not themselves significantly toxic; they have toxicities indistinguishable from common household dish liquids and shampoos,⁴⁵ including those used for cleaning oiled seabirds,^{46,47} and the majority, including those used in the *Deepwater Horizon* response, show neither androgen- nor estrogen-receptor activity.⁴⁸ Nevertheless, the use of dispersants involves adding more chemicals to an already impacted area, and the water under a recently dispersed oil slick is significantly transiently more toxic to organisms than under the undispersed slick, albeit because of the greater concentrations of oil in the water, not because of any increase in toxicity on an oil weight basis.^{47,48,50}

So, how should spill response coordinators decide when and where to use dispersants? Most responders rely on a net environmental benefit analysis, often abbreviated NEBA.^{51–55} At first glance, the concept seems oxymoronic: how can anything related to an oil spill have an environmental benefit? However, in actuality, the concept is very useful: everyone involved in a cleanup recognizes that an oil spill is a dreadful environmental insult and is working diligently to minimize adverse impacts and to remove the oil as quickly as possible. The question is whether a response tool will end up doing more harm than good, of whether there will be net environmental improvement despite potential collateral harm done in the short term by the response. Table 1 offers a comparison of the potential hazards and environmental fate of floating slicks and dispersed oils that need to be considered in such analyses.

The first hurdle for dispersants is to demonstrate their fundamental efficacy. In the United States, the U.S. Environmental Protection Agency (USEPA) maintains the National Oil and Hazardous Substances Pollution Contingency Plan Product Schedule⁵⁶ as part of the National Contingency Plan and lists chemical dispersants that may be authorized for use. Dispersants on the Product Schedule have demonstrated effectiveness; they can disperse at least 45% of Prudhoe Bay or South Louisiana crude oil in a standard swirling flask test.⁵⁷ The swirling flask test is one of several tests designed to discriminate between dispersants with different efficacies on a simple laboratory scale. It does this reasonably well (although the USEPA is considering revising it with a baffled flask test⁵⁸), but unfortunately the passing grade of 45% has often been assumed to indicate expected field performance. In fact, the test dramatically underestimates efficacy in the field, primarily due to the amount of energy it imparts to the floating oil and the volume available for diffusion. Tests in the OHMSETT facility,⁵⁹ a wave tank in New Jersey that is $200\ \text{m}$ long, $20\ \text{m}$ wide, and $2.5\ \text{m}$ deep, routinely measure dispersant efficiencies $>95\%$, even at low temperatures with ice in the water.⁶⁰

A second requirement for listing on the USEPA product schedule is that the acute toxicity of the dispersant to two reference species (silverside fish, *Menidia beryllina* (96 h), and mysid shrimp, *Americamysis bahia* (48 h)^{49,59}) be reported. During the *Deepwater Horizon* response, the USEPA required that dispersants “have a toxicity value less than or equal to (sic) 23.00 (sic) ppm LC_{50} toxicity value for *Menidia* or 18.00 ppm LC_{50} for *Mysidopsis* (*Americamysis*)”;⁶² the dispersants being used passed this hurdle.⁴⁹

As mentioned above, the toxicity of modern dispersants is usually so low as to likely have only minimal adverse effects at levels used in response operations (nominal aerial dispersant application rates are 5 gallons of dispersant per acre, $47\ \text{L/hectare}$;⁶³ diffusion into the top $20\ \text{cm}$ of seawater would give concentrations around $23\ \text{ppm}$, and of course further diffusion will continually lower the concentration). However, dispersed oil is significantly more toxic, with acute LC_{50} values more than an order of magnitude lower.⁴⁹ There has been some confusion around quantifying the toxicity of dispersed oil;^{64,65} acute toxicity arises from a general narcosis caused by dissolved hydrocarbons moving to the lipids of the test organism,^{66–68} so if estimates of oil concentrations include small droplets, the toxicity expressed on a per milligram hydrocarbon basis are lower (higher LC_{50}) than that for dissolved components. In any case, dispersants encourage solubility by increasing the surface-

Table 1

potential hazards and environmental fate of floating slick	potential hazards and environmental fate of dispersants and dispersed oil
<p>Floating oil can be lethal to birds or mammals that penetrate it. The oil reduces the insulating properties of feathers and fur and may be toxic if ingested during preening or grooming.^{112,122} Mild oiling may be transferred to eggs, chicks, and young.¹⁰⁷ Floating oil also likely kills small invertebrates, algae, fish eggs, and young that are at the sea surface under the slick.¹⁰⁸</p> <p>Floating oil is subject to photooxidation, which polymerizes polycyclic aromatic compounds to polar materials.^{110,111} This eventually leads to very persistent tarballs.¹¹² Beached oil undergoes a similar process, leading to very persistent "pavements".^{126,127}</p> <p>Transparent planktonic organisms may accumulate polycyclic aromatic compounds leached from slicks and beached oil and may be subject to phototoxicity in the surface layer of the sea.¹¹³ Floating oil absorbs water; it is not unusual for floating slicks to increase their volume by >50% in 24 h.^{114–116} This phenomenon makes dispersion more difficult but not impossible.¹¹⁷ Over several days, many floating oils emulsify, forming water-in-oil emulsions known as mousse.^{118–120} The encapsulated water no longer exchanges with bulk seawater, and biodegradation is likely even more nutrient- and oxygen-limited than in the floating slick. Mousse may be consumed by fish, turtles, etc. and also lead to tarballs.^{111,112}</p> <p>Small molecules in floating oil evaporate rapidly, becoming volatile organic compounds (VOCs).^{121,129} that can reach levels of concern for spill responders.¹²¹ Evaporated molecules may be destroyed by photochemistry¹²² or biodegradation.¹²³</p> <p>If it is not physically dispersed by storms or recovered mechanically, then an oil slick will likely beach on a shoreline. If it stays on the shoreline surface, then it may be possible to remove it by physical means, but storms will likely incorporate oil deep into sandy beaches,^{124,125} where, if left alone, it will likely remain for decades.^{126,127} Beached oil can be a major threat to turtle and shorebird nesting¹²⁸ and to mangroves¹³⁰ and marshes,¹³⁰ and recovery may take years.^{131,132}</p> <p>If the slick arrives at a shoreline, then biodegradation will be slow because of the high concentration of oil in comparison to the low concentrations of bioavailable nutrients in tidal flows. Biodegradation was too slow to measure directly in the absence of bioremediation in Prince William Sound following the Exxon Valdez spill,^{18,19} but even with effective bioremediation, the half-life of total detectable hydrocarbons was of the order of 10 weeks.^{18,19}</p>	<p>Dispersant application has the potential to create aerosols with potentially adverse effects on humans and wildlife. Such effects are seen only in the laboratory at quite high concentrations and with prolonged exposures.^{99–102} They are minimized by protective equipment for applicators and exclusion zones around application. Aerial application is very unlikely to be approved within several miles of a coast.</p> <p>The addition of dispersants puts additional chemicals into a polluted area. Nominal application rates of dispersants are 5 gallons per acre (47 L ha⁻¹) for surface spills,⁶³ equivalent to a dispersant/oil ratio of about 1:20. Subsea injection seems to be effective at much lower doses, perhaps 1:100 or less. Dispersants are composed of chemicals that are generally acceptable for food contact and are biodegradable,^{28,53,94} but when they are used at suboptimal doses, they may become incorporated into persistent tarballs.⁹⁶</p> <p>Dispersants may persist in the environment. Dispersants are complex mixtures of surfactants and solvents, and very few techniques can measure them all.¹⁰⁴ Much published work has focused on individual chemicals, but since all of the components are widely used in consumer products on a far greater scale than in dispersants, care must be taken in attributing detection to dispersant use.⁹⁷</p> <p>Dispersants may not penetrate heavy oils and may "roll-off" before they can be effective.^{103,105} Nevertheless, dispersants have been shown to be effective with many heavy oils,¹¹⁷ and new formulations are being developed to further this use.¹⁰⁶</p> <p>Suboptimal dispersant application may not disperse the oil but may hinder subsequent skimming operations.</p> <p>Several studies appear to show that dispersants do not stimulate biodegradation very much.^{139–141,367,8} Those experiments were based on a misunderstanding of the role of dispersants,³⁷ which is simply to disperse oil into tiny droplets that can diffuse apart. Such dilute small droplets, whether generated by dispersants or by low concentrations of oil, are degraded rapidly,^{36–38,78} and dispersants show no significant stimulatory effect. Dispersed oils that can re-coalesce into larger droplets, as occurs in laboratory experiments with more than a few parts per million oil,^{139–141} again show only a small stimulation of biodegradation by dispersants. A clear stimulation of biodegradation by dispersants (many fold) is seen only when dispersed oil at environmentally realistic concentrations^{29–36} is compared to an undispersed slick.³⁷ It is the latter that is the target of dispersants.</p> <p>Dispersants have been reported to be toxic to some bacteria.¹⁴² These experiments looked at a few isolated cultivars from beach sand rather than pelagic organisms likely to be exposed to dispersants. Dispersants had no inhibitory effects in experiments with pelagic microbes^{36–38,78} and were significantly less toxic than oil alone to <i>Vibrio fischeri</i> (now <i>Aliivibrio fischeri</i>)¹⁴³ in the Microtox test.¹⁴⁴</p> <p>Dispersed oil is potentially toxic to organisms close to the surface when the oil is initially dispersed. This is particularly true for small invertebrates, algae, fish eggs, and young that cannot swim away.¹⁰⁹ Nevertheless, measured dilution suggests that they will not be exposed for very long.^{29–36} The remarkably heterogeneous distribution of planktonic organisms, on all scales, probably has more influence on local populations than relatively small-scale mortality due to concentrated dispersions of oil.^{145,146} Planktonic microbial species respond remarkably rapidly, even to diel cycles.¹⁴⁷ Fish kills are rarely noted after dispersant use, presumably because fish and other nekton swim away from the dispersed oil.</p>
Dispersed polycyclic aromatic compounds may be accumulated by transparent planktonic organisms, which may then be subject to phototoxicity in the surface layer of the sea. ¹¹³	Dispersed polycyclic aromatic compounds may be accumulated by transparent planktonic organisms, which may then be subject to phototoxicity in the surface layer of the sea. ¹¹³
Dispersion slows evaporation, especially if the oil is dispersed subsea, as some was in the Deepwater Horizon response. The potentially toxic small molecules are retained in the water column until they are biodegraded or escape to the atmosphere over a much greater area due to diffusion at depth.	Dispersion slows evaporation, especially if the oil is dispersed subsea, as some was in the Deepwater Horizon response. The potentially toxic small molecules are retained in the water column until they are biodegraded or escape to the atmosphere over a much greater area due to diffusion at depth.
Dispersants are typically used far from shore in deep water (e.g., >3 miles ¹⁴⁸). Dispersed oil diffuses to sub parts per million levels and is very unlikely to reach a shoreline in noticeable quantities.	Dispersants are typically used far from shore in deep water (e.g., >3 miles ¹⁴⁸). Dispersed oil diffuses to sub parts per million levels and is very unlikely to reach a shoreline in noticeable quantities.
Dispersed oil dilutes to such low concentrations that biodegradation is rapid. Measured half-lives are in the days to few weeks time frame. ^{14,33–37} Even the four ring aromatic chrysene and its methyl-, dimethyl-, and ethyl- forms have half-lives on the order of a month. ³⁶ Nearshore waters from the Chukchi Sea, ⁷⁸ the North West Atlantic, ³⁶ and deepwater from Trondheim Fjord ³⁸ all contained enough nutrients for substantial biodegradation of a few parts per million oil in 60 days, and it is reasonable to extrapolate that further dilution in more oligotrophic waters would allow similar degradation on similar time scales.	Dispersed oil dilutes to such low concentrations that biodegradation is rapid. Measured half-lives are in the days to few weeks time frame. ^{14,33–37} Even the four ring aromatic chrysene and its methyl-, dimethyl-, and ethyl- forms have half-lives on the order of a month. ³⁶ Nearshore waters from the Chukchi Sea, ⁷⁸ the North West Atlantic, ³⁶ and deepwater from Trondheim Fjord ³⁸ all contained enough nutrients for substantial biodegradation of a few parts per million oil in 60 days, and it is reasonable to extrapolate that further dilution in more oligotrophic waters would allow similar degradation on similar time scales.

Table 1. continued

potential hazards and environmental fate of floating slick	potential hazards and environmental fate of dispersants and dispersed oil
<p>biodegradation of bulk oil in the Gulf of Mexico was very slow^{74,75} compared to that of dispersed oil.^{35,14}</p> <p>While oil hydrocarbons are essentially completely biodegradable (e.g., ref 36), many of the deeply colored molecules (resins, asphaltene, polars, etc.) are more resistant to biodegradation, although at least some are consumed.^{133,134} While these have minimal biological effects, the lifetime of these molecules in a sandy beach may be prolonged, especially if they have been entrained deep in a beach by storm action.^{124,132}</p> <p>Physical cleanup of beached oil can take weeks to years and requires hundreds to thousands of workers with their ancillary vehicles and support services.^{16,128,136}</p>	<p>While oil hydrocarbons are essentially completely biodegradable (e.g., ref 36), many of the deeply colored molecules (resins, asphaltene, polars, etc.) are more resistant to biodegradation, although at least some are consumed.^{133,134} Once the hydrocarbons have been degraded, these fractions lack oily characteristics and become essentially indistinguishable from other inert organic matter in the environment, such as humins.¹³⁵</p> <p>Optimal dispersant application for surface slicks uses planes that can carry 5000 gallons (19000 L) of dispersant, appropriate to treat 1000 acres (405 ha) of slick.⁶³ Depending on distances from airfields, several sorties can be flown per day, and spills from a tanker can be treated in a few days. Aerial spraying requires daylight (Figure 1).</p> <p>Subsea injection has the advantage of continuing 24 h a day, and the lower application rates mean that dispersant stocks will potentially last longer. If fully successful, oil from a subsea release may never reach the surface before it is biodegraded.¹⁰³</p>



Figure 1. An updated DC3C spraying dispersants on oil from the Deepwater Horizon blowout. The wingspan is 29 m. Reproduced with permission from Airborne Support.

to-volume ratio of the oil, and there is a potential for short-term toxic effects in a dispersed plume. The question is how significant these effects might be in the field. Canonical acute toxicity tests involve constant exposures for 48 or 96 h,⁶¹ but in a response at sea, the concentrations of oil will be dropping rapidly due to dilution by mixing and diffusion. As noted above, concentrations of dispersed oil drop to below 1 ppm within a few hours.^{29–33}

Only acute toxicity tests are required for listing under the National Contingency Plan, but of course chronic effects are also a real concern. As expected, the longer exposure required to see chronic effects allows lower concentrations of hydrocarbons to exert an effect, and typical acute-to-chronic ratios are 1:10, that is, it may only take 10% of the acute LC₅₀ to have a chronic EC₅₀.^{69–72} Again, these concentrations are for prolonged exposures, and it is not clear how these relate to the very low concentrations^{29–34} of dispersed oil that are found several days after dispersion.⁷³

As noted at the outset, dispersants were initially conceived as a tool for minimizing seabird mortality, and early use weighed that benefit against potential toxicity to planktonic species.²⁷ However, an additional substantial benefit has now been clearly documented: the biodegradation of dispersed oil is dramatically faster than that of oil in a slick or on a shoreline. Oil on shorelines of Prince William Sound, Alaska, had a half-life of a year or more,^{18–20} even with the substantial washing and bioremediation program.¹⁶ Tarballs and mousse associated with the Deepwater Horizon blowout had similar persistence in the environment.^{74,75} However, the biodegradation of dispersed oil is rapid and extensive.^{14,35–37}

The oil spill response community agrees that the best response to an oil spill would be to collect it from the environment before it reached a shoreline, and many response plans focus on this requirement by staging large amounts of equipment aimed at achieving this goal even in the face of a very large spill (e.g., refs 9–12). However, if oil cannot be collected, particularly if it is unsafe for responders to perform mechanical recovery or because of remote location or hours of daylight, then responders must look to other methods. It is important to recognize that time is of the essence: deciding not to use a response option today may preclude its use tomorrow. This phenomenon, the window-of-opportunity,⁷⁶ is particularly relevant to the use of dispersants because as oil weathers by

evaporation and absorption of underlying water, it becomes progressively more and more difficult to disperse with dispersants. (As an aside, dispersants incorporated into relatively fresh oil will help the dispersion of that oil even after some time if conditions are initially too calm for immediate dispersion,⁷⁷ a potential problem for requirements that dispersants be seen to be effective on a trial basis before large-scale application can begin.) Responders must weigh the potential additional short-term toxicity likely incurred immediately under a dispersed surface slick against the benefit of protecting diving birds and animals and having the oil removed from the environment by biodegradation on a time scale of a few weeks rather than years with a vastly smaller human footprint of spill response. The speed of biodegradation is particularly important if the over-riding concern about dispersant use is the potential local increase in toxicity; beached oil and undispersed mousse leach hydrocarbons and have their own potential environmental impacts for a prolonged period. It would also be prudent to bear in mind the environmental impact of large shoreline cleanup operations, which often involve hundreds of workers and the ancillary impacts of their support services. There is also the potential legacy of the final disposal of the oil, which may well involve burial at a secure landfill rather than combustion or biodegradation. Finally, while not an environmental impact, the economic impacts of an oiled marina or shoreline also need to be weighed as responders decide the most appropriate spill-response.

■ CONCLUDING REMARKS

In the final analysis, some accidents occur so close to shore that oil will undoubtedly reach the shoreline and most likely require some physical cleanup, perhaps followed by bioremediation. However, if the release is in deep water, then it ought to be possible to mobilize dispersants to keep bulk oil from ever reaching a shoreline. If oil is successfully dispersed into the water column, then it is likely that biodegradation will remove the vast majority of it in weeks to months, even in the Arctic and Antarctic.⁷⁸ What remains will likely be finely dispersed fragments of nonoily (to the touch) material depleted of hydrocarbons and rich in asphaltic materials and saturated biomarkers such as the hopanes.^{36,79,80}

Many questions remain to be answered:

- How does the density of dispersed oil change as biodegradation proceeds? Alkanes are much lighter than water,⁸¹ even at high pressure,⁸² as are cyclic alkanes and monoaromatics. However, larger aromatic hydrocarbons, such as chrysene, have densities greater than 1,⁸³ as do the resins and asphaltenes.^{84,85} Since biodegradation preferentially removes alkanes, initially buoyant droplets will become neutral and eventually sink. Is this partially degraded oil further metabolized once deposited on the surface sediment at depth? Reports of substantial amounts of fossil (radiocarbon silent) carbon on the surface sediment at depth⁸⁶ could be either unmetabolized oil molecules or the biomass of organisms degrading the oil or, more likely, both. As noted above, some molecules, such as the hopanes, seem very resistant to biodegradation and likely remain with very biodegraded oil (and degrading biomass) as a fingerprint of the initial source.^{36,75,79,80}

- What fraction of the oil carbon is mineralized to CO₂ in the initial biodegradation, and what fraction is incorporated into biomass? Classical experiments with aerobes growing on glucose suggest a biomass yield of about 50%,⁸⁷ but what is the fate of that biomass? Levy and Lee⁸⁸ propose that it is the base for substantial fisheries offshore Atlantic Canada. Chemical analysis of the radiocarbon silent material reported by Chanton et al.⁸⁶ will shed light on this question.
- What role does microbial succession play in the biodegradation of oil? Such succession was clearly seen in the Gulf of Mexico following the *Deepwater Horizon* release,^{87–92} but how did it relate to the chemical composition of the residual oil or to the nutrient levels in the water? Do dispersants affect this succession?
- How rapidly are dispersant components degraded in the sea? Early work established the biodegradation of nonionic surfactants in seawater,⁹³ and dioctylsulfosuccinate is known to be biodegradable⁹⁴ and clearly was being degraded close to the *Deepwater Horizon* spill site where it was being applied in the Corexit dispersant.⁹⁵ Nevertheless, traces of dioctylsulfosuccinate have been found far from the *Deepwater Horizon* accident;⁹⁶ was that associated with dispersant application? Traces found close to shore are more likely related to stormwater discharges.⁹⁵ Small quantities associated with tarballs⁹⁸ are likely the result of suboptimal dispersant application and highlight the need to apply an effective amount of dispersant if its benefits are to be achieved.
- Is biodegradation at depth (>1500 m) fundamentally distinct from biodegradation at the surface? Early work suggested that it is not,¹³⁷ but that work was clearly limited in its experimental tools, and there is much to learn. There is no doubt that active hydrocarbon-degrading microbial communities, both aerobic and anaerobic, are present in deep sea sediments.¹³⁸

Already, however, we know enough from laboratory, mesocosm, and field experience to say that dispersed oil is degraded much more rapidly than undispersed oil, likely orders of magnitude more rapidly. This is the key piece of information that seems to be overlooked in most discussions of the potential adverse impacts of using dispersants. Even if there is an adverse local impact of dispersed oil, it will not last long. On the other hand, oil that reaches a shoreline may be there for years.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) *Statistical Review of World Energy*; BP, 2014. <http://www.bp.com/en/global/corporate/about-bp/energy-economics/statistical-review-of-world-energy.html>.

- (2) National Research Council Oil in the Sea III: Inputs, Fates, and Effects; National Academies Press: Washington, DC, 2003.
- (3) Musk, S. Trends in oil spills from tankers and ITOPF non-tanker attended incidents, 2012. <http://www.itopf.com/knowledge-resources/documents-guides/document/trends-in-oil-spills-from-tankers-and-itopf-non-tanker-attended-incidents-2012/>.
- (4) Lubchenco, J.; McNutt, M. K.; Dreyfus, G.; Murawski, S. A.; Kennedy, D. M.; Anastas, P. T.; Chu, S.; Hunter, T. Science in support of the Deepwater Horizon response. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 20212–20221.
- (5) Tissot, B. P.; Welte, D. H. *Petroleum Formation and Occurrence*; Springer: Berlin, 1984.
- (6) Prince, R. C.; Gramain, A.; McGenity, T. J. Prokaryotic hydrocarbon degraders. In *Handbook of Hydrocarbon and Lipid Microbiology*; Timmis, K. N., Ed.; Springer-Verlag: Berlin, 2010; pp 1672–1692.
- (7) Prince, R. C. Eukaryotic hydrocarbon degraders. In *Handbook of Hydrocarbon and Lipid Microbiology*; Timmis, K. N., Ed.; Springer-Verlag: Berlin, 2010; pp 2066–2078.
- (8) Fingas, M. *The Basics of Oil Spill Cleanup*; CRC Press: Boca Raton, FL, 2012.
- (9) Aleska Oil Spill Prevention, Response and Preparedness, 2014. <http://www.aleska-pipe.com/SafetyEnvironment/PreventionAndResponse>.
- (10) San Francisco Oil Spill Contingency Plan, 2014. https://www.dfg.ca.gov/ospr/san_francisco_plan.aspx.
- (11) Thames Oil Spill Clearance Association, 2014. <http://www.pla.co.uk/About-Us/TOSCA>.
- (12) ITOPF Country Profiles, 2014. <http://www.itopf.com/knowledge-resources/countries-regions/>.
- (13) Atlas, R. M.; Bartha, R. Degradation and mineralization of petroleum in sea water: limitation by nitrogen and phosphorus. *Biotechnol. Bioengineer.* **1972**, *14*, 309–318.
- (14) Bælum, J.; Borglin, S.; Chakraborty, R.; Fortney, J. L.; Lamendella, R.; Mason, O. U.; Auer, M.; Zemla, M.; Bill, M.; Conrad, M. E.; Malfatti, S. A.; Tringe, S. G.; Holman, H. Y.; Hazen, T. C.; Jansson, J. K. Deep-sea bacteria enriched by oil and dispersant from the Deepwater Horizon spill. *Environ. Microbiol.* **2012**, *14*, 2405–2416.
- (15) Garcia, H. E.; Locarnini, R. A.; Boyer, T. P.; Antonov, J. I.; Zweng, M. M.; Baranova, O. K.; Johnson, D. R. *World Ocean Atlas 2009: Nutrients (Phosphate, Nitrate, And Silicate)*, NOAA Atlas NESDIS 71; Levitus, S., Ed.; U.S. Government Printing Office: Washington, DC, 2010; Vol. 4.
- (16) Nauman, S. A. Shoreline cleanup: equipment and operations. In *International Oil Spill Conference Proceedings*; American Petroleum Institute: Washington, DC, 1991; pp 141–147.
- (17) Lindstrom, J. E.; Prince, R. C.; Clark, J. R.; Grossman, M. J.; Yeager, T. R.; Braddock, J. F.; Brown, E. J. Microbial populations and hydrocarbon biodegradation potentials in fertilized shoreline sediments affected by the T/V Exxon Valdez oil spill. *Appl. Environ. Microbiol.* **1991**, *57*, 2514–2522.
- (18) Bragg, J. R.; Prince, R. C.; Harner, E. J.; Atlas, R. M. Effectiveness of bioremediation for the Exxon Valdez oil spill. *Nature* **1994**, *368*, 413–418.
- (19) Prince, R. C.; Clark, J. R.; Lindstrom, J. E.; Butler, E. L.; Brown, E. J.; Winter, G.; Grossman, M. J.; Parrish, R. R.; Bare, R. E.; Braddock, J. F.; Steinhauer, W. G.; Douglas, G. S.; Kennedy, J. M.; Barter, P. J.; Bragg, J. R.; Harner, E. J.; Atlas, R. M. Bioremediation of the Exxon Valdez oil spill: monitoring safety and efficacy. In *Hydrocarbon Remediation*; Hinchey, R. E.; Alleman, B. C.; Hoeppe, R. E.; Miller, R. N., Eds.; Lewis Publishers: Boca Raton, FL, 1994; pp 107–124.
- (20) Prince, R. C.; Bragg, J. R. Shoreline bioremediation following the Exxon Valdez oil spill in Alaska. *Biorem. J.* **1997**, *1*, 97–104.
- (21) Page, G. W.; Carter, H. R.; Ford, R. G. Numbers of seabirds killed or debilitated in the 1986 Apex Houston oil spill in central California. *Studies Avian Biol.* **1990**, *14*, 164–174.
- (22) Murphy, S. M.; Day, R. H.; Wiens, J. A.; Parker, K. R. Effects of the Exxon Valdez oil spill on birds: comparisons of pre-and post-spill surveys in Prince William Sound, Alaska. *Condor* **1997**, *99*, 299–313.
- (23) Henkel, J. R.; Sigel, B. J.; Taylor, C. M. Large-scale impacts of the Deepwater Horizon oil spill: can local disturbance affect distant ecosystems through migratory shorebirds? *BioScience* **2012**, *62*, 676–685.
- (24) Chasse, C. The ecological impact on and near shores by the Amoco Cadiz oil spill. *Mar. Pollut. Bull.* **1978**, *9*, 298–301.
- (25) Neuparth, T.; Moreira, S. M.; Santos, M. M.; Reis-Henriques, M. A. Review of oil and HNS accidental spills in Europe: identifying major environmental monitoring gaps and drawing priorities. *Mar. Pollut. Bull.* **2012**, *64*, 1085–1095.
- (26) Anink, P. J.; Hunt, D. R.; Roberts, D. E.; Jacobs, N. E. Oil spill in Botany Bay: short term effects and long term implications. *Wetlands (Australia)* **1985**, *5*, 32–41.
- (27) National Research Council Oil Spill Dispersants: Efficacy and Effects; National Academies Press: Washington, DC, 2005.
- (28) COREXIT® Ingredients; Nalco: Sugar Land, TX, 2014. <http://www.nalcoesllc.com/nes/1602.htm>.
- (29) Cormack, D.; Nichols, J. A. The concentrations of oil in sea water resulting from natural and chemically induced dispersion of oil slicks. In *International Oil Spill Conference Proceedings*; American Petroleum Institute: Washington, DC, 1977; pp 381–385.
- (30) Lichtenthaler, R. G.; Daling, P. S. Dispersion of chemically treated crude oil in Norwegian offshore waters. In *International Oil Spill Conference Proceedings*; American Petroleum Institute: Washington, DC, 1983; pp 7–14.
- (31) McAuliffe, C. D.; Johnson, J. C.; Greene, S. H.; Canevari, G. P.; Searl, T. D. Dispersion and weathering of chemically treated crude oils on the ocean. *Environ. Sci. Technol.* **1980**, *14*, 1509–1518.
- (32) BenKinney, M.; Brown, J.; Mudge, S.; Russell, M.; Nevin, A.; Huber, C. Monitoring effects of aerial dispersant application during the MC252 Deepwater Horizon Incident. In *International Oil Spill Conference Proceedings*; American Petroleum Institute: Washington, DC, 2011; p 368.
- (33) Bejarano, A. C.; Levine, E.; Mearns, A. J. Effectiveness and potential ecological effects of offshore surface dispersant use during the Deepwater Horizon oil spill: a retrospective analysis of monitoring data. *Environ. Monit. Assess.* **2013**, *185*, 10281–10295.
- (34) Wade, T. L.; Sweet, S. T.; Sericano, J. L.; Guinasso, N. L.; Diercks, A. R.; Highsmith, R. C.; Asper, V. L.; Joung, D. J.; Shiller, A. M.; Lohrenz, S. E.; Joye, S. B. Analyses of water samples from the Deepwater Horizon oil spill: documentation of the subsurface plume. In *Monitoring and Modeling the Deepwater Horizon Oil Spill: A Record-Breaking Enterprise*; Liu, Y.; Macfadyen, A.; Ji, Z. J.; Weisberg, R. H., Eds.; American Geophysical Union: Washington, DC, 2011; pp 77–82.
- (35) Hazen, T. C.; Dubinsky, E. A.; DeSantis, T. Z.; Andersen, G. L.; Piceno, Y. M.; Singh, N.; Jansson, J. K.; Probst, A.; Borglin, S. E.; Fortney, J. L.; Stringfellow, W. T.; Bill, M.; Conrad, M. S.; Tom, L. M.; Chavarria, K. L.; Alusi, T. R.; Lamendella, R.; Joyner, D. C.; Spier, C.; Bælum, J.; Auer, M.; Zemla, M. L.; Chakraborty, R.; Sonnenthal, E. L.; D'haeseleer, P.; Holman, H. N.; Osman, S.; Lu, Z.; Van Nostrand, J. D.; Deng, Y.; Zhou, J.; Mason, O. U. Deep-sea oil plume enriches indigenous oil-degrading bacteria. *Science* **2010**, *330*, 204–208.
- (36) Prince, R. C.; McFarlin, K. M.; Butler, J. D.; Febbo, E. J.; Wang, F. C. Y.; Nedwed, T. J. The primary biodegradation of dispersed crude oil in the sea. *Chemosphere* **2013**, *90*, 521–526.
- (37) Prince, R. C.; Butler, J. D. A protocol for assessing the effectiveness of oil spill dispersants in stimulating the biodegradation of oil. *Environ. Sci. Pollut. Res.* **2014**, *21*, 9506–9510.
- (38) Brakstad, O. G.; Nordtug, T.; Throne-Holst, M. Biodegradation of dispersed Macondo oil in seawater at low temperature and different oil droplet sizes. *Mar. Pollut. Bull.* **2015**, *93*, 144–152.
- (39) Zahed, M. A.; Aziz, H. A.; Isa, M. H.; Mohajeri, L.; Mohajeri, S.; Kutty, S. R. M. Kinetic modeling and half-life study on bioremediation of crude oil dispersed by Corexit 9500. *J. Hazard. Mater.* **2011**, *185*, 1027–1031.
- (40) Harris, C. The Braer incident: Shetland Islands, January 1993. In *International Oil Spill Conference Proceedings*; American Petroleum Institute: Washington, DC, 1995; pp 813–819.

- (41) Law, R. J.; Kelly, C. The impact of the *Sea Empress* oil spill. *Aquat. Living Resour.* **2004**, *17*, 389–394.
- (42) Henry, C. Review of dispersant use in US Gulf of Mexico waters since the Oil Pollution Act of 1990. In *International Oil Spill Conference Proceedings*; American Petroleum Institute: Washington, DC, 2005; pp 439–442.
- (43) *Global Dispersant Stockpile*; Oil Spill Response Ltd.: London, 2014. <http://www.oilspillresponse.com/services-landing/global-dispersant-stockpile>.
- (44) *ExxonMobil Oil Spill Dispersant Guidelines*, 2008. ccrc.unh.edu/sites/ccrc.unh.edu/files/exxonmobil_dispersant_guidelines_2008.pdf.
- (45) Word, J. Q.; Clark, J. R.; Word, L. S. Comparison of the acute toxicity of Corexit 9500 and household cleaning products. *Hum. Ecol. Risk Assess.* **2014**, *21*, 707–725.
- (46) Russell, M.; Holcomb, J.; Berkner, A. 30-years of oiled wildlife response statistics. Proceedings of the 7th International Effects of Oil on Wildlife Conference, Hamburg, Germany, October 14–16, 2003; pp 14–16. pszhhw.bird-rescue.org/pdfs/IBRRC_stats_paper.pdf.
- (47) *Best Practices for Migratory Bird Care During Oil Spill Response*; USFWS: Anchorage, AK, 2003. www.fws.gov/contaminants/fws_osc/05/fwscontingencyappendices/D-BestPracticesMigBirds/BestPracticesmar04rev.pdf.
- (48) Judson, R. S.; Martin, M. T.; Reif, D. M.; Houck, K. A.; Knudsen, T. B.; Rotroff, D. M.; Xia, M.; Sakamuru, S.; Huang, R.; Shinn, P.; Austin, C. P.; Kavlock, R. J.; Dix, D. J. Analysis of eight oil spill dispersants using rapid, *in vitro* tests for endocrine and other biological activity. *Environ. Sci. Technol.* **2010**, *44*, 5979–5985.
- (49) Hemmer, M. J.; Barron, M. G.; Greene, R. M. Comparative toxicity of eight oil dispersants, Louisiana sweet crude oil (LSC), and chemically dispersed LSC to two aquatic test species. *Environ. Toxicol. Chem.* **2011**, *30*, 2244–2252.
- (50) Gardiner, W. W.; Word, J. Q.; Word, J. D.; Perkins, R. A.; McFarlin, K. M.; Hester, B. W.; Word, L. S.; Ray, C. M. The acute toxicity of chemically and physically dispersed crude oil to key arctic species under arctic conditions during the open water season. *Environ. Toxicol. Chem.* **2013**, *32*, 2284–2300.
- (51) Baker, J. M. Net environmental benefit analysis for oil spill response. In *International Oil Spill Conference Proceedings*; American Petroleum Institute: Washington, DC, 1995; pp 611–614.
- (52) Chapman, H.; Purnell, K.; Law, R. J.; Kirby, M. F. The use of chemical dispersants to combat oil spills at sea: a review of practice and research needs in Europe. *Mar. Pollut. Bull.* **2007**, *54*, 827–838.
- (53) Kirby, M. F.; Law, R. J. Oil spill treatment products approval: the UK approach and potential application to the Gulf region. *Mar. Pollut. Bull.* **2008**, *56*, 1243–1247.
- (54) *API Net Environmental Benefit Analysis for Effective Oil Spill Preparedness and Response*, 2013. www.api.org/~media/Files/EHS/Clean_Water/Oil_Spill_Prevention/NEBA/NEBA-Net-Environmental-Benefit-Analysis-July-2013.pdf.
- (55) McCay, D. F.; Graham, E. Quantifying tradeoffs-net environmental benefits of dispersant use. In *International Oil Spill Conference Proceedings*; American Petroleum Institute: Washington, DC, 2014; pp 762–775.
- (56) *USEPA Alphabetical List of NCP Product Schedule (Products Available for Use During an Oil Spill)*, 2014 <http://www2.epa.gov/emergency-response/alphabetical-list-ncp-product-schedule-products-available-use-during-oil-spill>.
- (57) *USEPA Swirling Flask Dispersant Effectiveness Test, Revised Standard Dispersant Toxicity Test, and Bioremediation Agent Effectiveness Test*, 2006. <http://www.gpo.gov/fdsys/pkg/CFR-2006-title40-vol27/xml/CFR-2006-title40-vol27-part300-appC.xml>.
- (58) *USEPA National Oil and Hazardous Substances Pollution Contingency Plan: Proposed Rule*, 2015. <https://www.federalregister.gov/articles/2015/01/22/2015-00544/national-oil-and-hazardous-substances-pollution-contingency-plan>.
- (59) *Ohmsett—National Oil Spill Response Research Facility*; BSSE: Washington, DC, 2014. <http://www.bsee.gov/Technology-and-Research/Ohmsett/index/>.
- (60) Belore, R. C.; Trudel, K.; Mullin, J. V.; Guarino, A. Large-scale cold water dispersant effectiveness experiments with Alaskan crude oils and Corexit 9500 and 9527 dispersants. *Mar. Pollut. Bull.* **2009**, *58*, 118–128.
- (61) *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms*, 5th ed.; USEPA: Washington, DC, 2002. http://water.epa.gov/scitech/methods/cwa/wet/disk2_index.cfm.
- (62) *Dispersant Monitoring and Assessment Directive – Addendum*; USEPA: Washington, DC, 2010. <http://www.epa.gov/bpspill/dispersants/directive-addendum2.pdf>.
- (63) *Dispersant Aerial Application Systems: Airborne Support Incorporated*; Clean Gulf Associates: New Orleans, LA, 2014. <http://www.cleangulfassoc.com/equipment/all/dispersant-aerial-application>.
- (64) Coelho, G.; Clark, J.; Aurand, D. Toxicity testing of dispersed oil requires adherence to standardized protocols to assess potential real world effects. *Environ. Pollut.* **2013**, *177*, 185–188.
- (65) Lewis, M. M.; Pryor, R. Toxicities of oils, dispersants and dispersed oils to algae and aquatic plants: Review and database value to resource sustainability. *Environ. Pollut.* **2013**, *180*, 345–367.
- (66) McGrath, J. A.; Parkerton, T. F.; Hellweger, F. L.; Di Toro, D. M. Validation of the narcosis target lipid model for petroleum products: gasoline as a case study. *Environ. Toxicol. Chem.* **2005**, *24*, 2382–2394.
- (67) Di Toro, D. M.; McGrath, J. A.; Stubblefield, W. A. Predicting the toxicity of neat and weathered crude oil: Toxic potential and the toxicity of saturated mixtures. *Environ. Toxicol. Chem.* **2007**, *26*, 24–36.
- (68) McCarty, L. S.; Arnot, J. A.; Mackay, D. Evaluation of critical body residue data for acute narcosis in aquatic organisms. *Environ. Toxicol. Chem.* **2013**, *32*, 2301–2314.
- (69) Länge, R. R.; Hutchinson, T. H.; Scholz, N.; Solbé, J. Analysis of the ECETOC aquatic toxicity (EAT) database II—comparison of acute to chronic ratios for various aquatic organisms and chemical substances. *Chemosphere* **1998**, *36*, 115–127.
- (70) Roex, E. W.; Van Gestel, C. A.; Van Wezel, A. P.; Van Straalen, N. M. Ratios between acute aquatic toxicity and effects on population growth rates in relation to toxicant mode of action. *Environ. Toxicol. Chem.* **2000**, *19*, 685–693.
- (71) Raimondo, S.; Montague, B. J.; Barron, M. G. Determinants of variability in acute to chronic toxicity ratios for aquatic invertebrates and fish. *Environ. Toxicol. Chem.* **2007**, *26*, 2019–2023.
- (72) Swigert, J. P.; Lee, C.; Wong, D. C. L.; Podhasky, P. Aquatic hazard and biodegradability of light and middle atmospheric distillate petroleum streams. *Chemosphere* **2014**, *108*, 1–9.
- (73) Landrum, P. F.; Chapman, P. M.; Neff, J.; Page, D. S. Influence of exposure and toxicokinetics on measures of aquatic toxicity for organic contaminants: a case study review. *Integr. Environ. Assess. Manage.* **2013**, *9*, 196–210.
- (74) Aeppli, C.; Nelson, R. K.; Radovic, J. R.; Carmichael, C. A.; Valentine, D. L.; Reddy, C. M. Recalcitrance and degradation of petroleum biomarkers upon abiotic and biotic natural weathering of Deepwater Horizon oil. *Environ. Sci. Technol.* **2014**, *48*, 6726–6734.
- (75) Yin, F.; John, G. F.; Hayworth, J. S.; Clement, T. P. Long-term monitoring data to describe the fate of polycyclic aromatic hydrocarbons in Deepwater Horizon oil submerged off Alabama's beaches. *Sci. Total Environ.* **2015**, *508*, 46–56.
- (76) Nordvik, A. B. The technology windows-of-opportunity for marine oil spill response as related to oil weathering and operations. *Spill Sci. Technol. Bull.* **1995**, *2*, 17–46.
- (77) Lewis, A. B.; Trudel, K.; Belore, R. C.; Mullin, J. V. Large-scale dispersant leaching and effectiveness experiments with oils on calm water. *Mar. Pollut. Bull.* **2010**, *60*, 244–254.
- (78) McFarlin, K. M.; Prince, R. C.; Perkins, R.; Leigh, M. B. Biodegradation of dispersed oil in arctic seawater at -1°C . *PLoS One* **2014**, *9*, e84297.
- (79) Ourisson, G.; Albrecht, P. Hopanoids. 1. Geohopanoids: the most abundant natural products on Earth? *Acc. Chem. Res.* **1992**, *25*, 398–402.

- (80) Valentine, D. L.; Fisher, G. B.; Bagby, S. C.; Nelson, R. K.; Reddy, C. M.; Sylva, S. P.; Woo, M. A. Fallout plume of submerged oil from *Deepwater Horizon*. *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111*, 15906–15911.
- (81) Queimada, A. J.; Quinones-Cisneros, S. E.; Marrucho, I. M.; Coutinho, J. A. P.; Stenby, E. H. Viscosity and liquid density of asymmetric hydrocarbon mixtures. *Int. J. Thermophys.* **2003**, *24*, 1221–1239.
- (82) Liu, K.; Wu, Y.; McHugh, M. A.; Baled, H.; Enick, R. M.; Morreale, B. D. Equation of state modeling of high-pressure, high-temperature hydrocarbon density data. *J. Supercrit. Fluids* **2010**, *55*, 701–711.
- (83) Wakeham, W. A.; Cholakov, G. S.; Stateva, R. P. Liquid density and critical properties of hydrocarbons estimated from molecular structure. *J. Chem. Eng. Data* **2002**, *47*, 559–570.
- (84) Alboudwarej, H.; Beck, J.; Svrcek, W. Y.; Yarranton, H. W.; Akbarzadeh, K. Sensitivity of asphaltene properties to separation techniques. *Energy Fuels* **2002**, *16*, 462–469.
- (85) Barrera, D. M.; Ortiz, D. P.; Yarranton, H. W. Molecular weight and density distributions of asphaltenes from crude oils. *Energy Fuels* **2013**, *27*, 2474–2487.
- (86) Chanton, J.; Zhao, T.; Rosenheim, B. E.; Joye, S. B.; Bosman, S.; Brunner, C. A.; Yeager, K. M.; Diercks, A. R.; Hollander, D. Using natural abundance radiocarbon to trace the flux of petrocarbon to the seafloor following the *Deepwater Horizon* oil spill. *Environ. Sci. Technol.* **2014**, *49*, 847–854.
- (87) Shiloach, J.; Fass, R. Growing *E. coli* to high cell density—a historical perspective on method development. *Biotechnol. Adv.* **2005**, *23*, 345–57.
- (88) Levy, E. M.; Lee, K. Potential contribution of natural hydrocarbon seepage to benthic productivity and the fisheries of Atlantic Canada. *Can. J. Fish. Aquat. Sci.* **1988**, *45*, 349–352.
- (89) Kostka, J. E.; Prakash, O.; Overholt, W. A.; Green, S. J.; Freyer, G.; Canion, A.; Delgadino, J.; Norton, N.; Hazen, T. C.; Huettel, M. Hydrocarbon-degrading bacteria and the bacterial community response in Gulf of Mexico beach sands impacted by the *Deepwater Horizon* oil spill. *Appl. Environ. Microbiol.* **2011**, *77*, 7962–7974.
- (90) Dubinsky, E. A.; Conrad, M. E.; Chakraborty, R.; Bill, M.; Borglin, S. E.; Hollibaugh, J. T.; Mason, O. U.; Piceno, Y. M.; Reid, F. C.; Stringfellow, W. T.; Tom, L. M.; Hazen, T. C.; Andersen, G. L. Succession of hydrocarbon-degrading bacteria in the aftermath of the *Deepwater Horizon* oil spill in the Gulf of Mexico. *Environ. Sci. Technol.* **2013**, *47*, 10860–10867.
- (91) Lamendella, R.; Strutt, S.; Borglin, S.; Chakraborty, R.; Tas, N.; Mason, O. U.; Hultman, J.; Prestat, E.; Hazen, T. C.; Jansson, J. K. Assessment of the *Deepwater Horizon* oil spill impact on Gulf coast microbial communities. *Front. Microbiol.* **2014**, *5*, 130.
- (92) Rodriguez-R, L. M.; Overholt, W. A.; Hagan, C.; Huettel, M.; Kostka, J. E.; Konstantinidis, K. T. Microbial community successional patterns in beach sands impacted by the *Deepwater Horizon* oil spill. *ISME J.* **2015**, DOI: 10.1038/ismej.2015.5.
- (93) Uña, G. V.; García, M. J. N. Biodegradation of non-ionic dispersants in sea-water. *Eur. J. Appl. Microbiol. Biotechnol.* **1983**, *18*, 315–319.
- (94) Cordon, T. C.; Maurer, E. W.; Stirton, A. J. The course of biodegradation of anionic detergents by analyses for carbon, methylene blue active substance and sulfate ion. *J. Am. Oil Chem. Soc.* **1970**, *47*, 203–206.
- (95) Gray, J. L.; Kanagy, L. K.; Furlong, E. T.; Kanagy, C. J.; McCoy, J. W.; Mason, A.; Lauenstein, G. Presence of the Corexit component dioctyl sodium sulfosuccinate in Gulf of Mexico waters after the 2010 *Deepwater Horizon* oil spill. *Chemosphere* **2014**, *95*, 124–130.
- (96) Kujawinski, E. B.; Kido Soule, M. C.; Valentine, D. L.; Boysen, A. K.; Longnecker, K.; Redmond, M. C. Fate of dispersants associated with the *Deepwater Horizon* oil spill. *Environ. Sci. Technol.* **2011**, *45*, 1298–1306.
- (97) Hayworth, J. S.; Clement, T. P. Provenance of COREXIT-related chemical constituents found in nearshore and inland Gulf Coast waters. *Mar. Pollut. Bull.* **2012**, *64*, 2005–2014.
- (98) White, H. K.; Lyons, S. L.; Harrison, S. J.; Findley, D. M.; Liu, Y.; Kujawinski, E. B. Long-term persistence of dispersants following the *Deepwater Horizon* oil spill. *Environ. Sci. Technol. Lett.* **2014**, *1*, 295–299.
- (99) Roberts, J. R.; Reynolds, J. S.; Thompson, J. A.; Zacccone, E. J.; Shimko, M. J.; Goldsmith, W. T.; Jackson, M.; McKinney, W.; Frazer, D. G.; Kenyon, A.; Kashon, M. L.; Piedimonte, G.; Castranova, V.; Fedan, J. S. Pulmonary effects after acute inhalation of oil dispersant (COREXIT EC9500A) in rats. *J. Toxicol. Environ. Health, Part A* **2011**, *74*, 1381–1396.
- (100) Krajnak, K.; Kan, H.; Waugh, S.; Miller, G. R.; Johnson, C.; Roberts, J. R.; Goldsmith, W. T.; Jackson, M.; McKinney, W.; Frazer, D.; Kashon, M. L.; Castranova, V. Acute effects of COREXIT EC9500A on cardiovascular functions in rats. *J. Toxicol. Environ. Health, Part A* **2011**, *74*, 1397–1404.
- (101) Sriram, K.; Lin, G. X.; Jefferson, A. M.; Goldsmith, W. T.; Jackson, M.; McKinney, W.; Frazer, D. G.; Robinson, V. A.; Castranova, V. Neurotoxicity following acute inhalation exposure to the oil dispersant COREXIT EC9500A. *J. Toxicol. Environ. Health, Part A* **2011**, *74*, 1405–1418.
- (102) Anderson, S. E.; Franko, J.; Lukomska, E.; Meade, B. J. Potential immunotoxicological health effects following exposure to COREXIT 9500A during cleanup of the *Deepwater Horizon* oil spill. *J. Toxicol. Environ. Health, Part A* **2011**, *74*, 1419–1430.
- (103) Johansen, Ø.; Brandvik, P. J.; Farooq, U. Droplet breakup in subsea oil releases—Part 2: Predictions of droplet size distributions with and without injection of chemical dispersants. *Mar. Pollut. Bull.* **2013**, *73*, 327–335.
- (104) Place, B. J.; Perkins, M. J.; Sinclair, E.; Barsamian, A. L.; Blakemore, P. R.; Field, J. A. Trace analysis of surfactants in Corexit oil dispersant formulations and seawater. *Deep-Sea Res.* **2014**, DOI: 10.1016/j.dsr.2014.01.015.
- (105) Canevari, G. P. The effect of crude oil composition on dispersant performance. In *International Oil Spill Conference Proceedings*; American Petroleum Institute: Washington, DC, 1985; pp 441–444.
- (106) Nedwed, T.; Canevari, G. P.; Clark, J. R.; Belore, R. New dispersant delivered as a gel. In *International Oil Spill Conference Proceedings*; American Petroleum Institute: Washington, DC, 2005; pp 121–125.
- (107) Finch, B. E.; Wooten, K. J.; Smith, P. N. Embryotoxicity of weathered crude oil from the Gulf of Mexico in mallard ducks (*Anas platyrhynchos*). *Environ. Toxicol. Chem.* **2011**, *30*, 1885–1891.
- (108) Irie, K.; Kawaguchi, M.; Mizuno, K.; Song, J. Y.; Nakayama, K.; Kitamura, S. I.; Murakami, Y. Effect of heavy oil on the development of the nervous system of floating and sinking teleost eggs. *Mar. Pollut. Bull.* **2011**, *63*, 297–302.
- (109) Almeda, R.; Baca, S.; Hyatt, C.; Buskey, E. J. Ingestion and sublethal effects of physically and chemically dispersed crude oil on marine planktonic copepods. *Ecotoxicology* **2014**, *23*, 988–1003.
- (110) Garrett, R. M.; Pickering, I. J.; Haith, C. E.; Prince, R. C. Photooxidation of crude oils. *Environ. Sci. Technol.* **1998**, *32*, 3719–3723.
- (111) Aeppli, C.; Carmichael, C. A.; Nelson, R. K.; Lemkau, K. L.; Graham, W. M.; Redmond, M. C.; Valentine, D. L.; Reddy, C. M. Oil weathering after the *Deepwater Horizon* disaster led to the formation of oxygenated residues. *Environ. Sci. Technol.* **2012**, *46*, 8799–8807.
- (112) Goodman, R. Tar balls: the end state. *Spill Sci. Technol. Bull.* **2003**, *8*, 117–121.
- (113) Barron, M. G.; Carls, M. G.; Short, J. W.; Rice, S. D.; Heintz, R. A.; Rau, M.; Di Giulio, R. Assessment of the phototoxicity of weathered Alaska North Slope crude oil to juvenile pink salmon. *Chemosphere* **2005**, *60*, 105–110.
- (114) Payne, J. R.; Clayton, J. R.; McNabb, G. D.; Kirstein, B. E. Exxon Valdez oil weathering fate and behavior: model predictions and field observations 1. In *International Oil Spill Conference Proceedings*; American Petroleum Institute: Washington, DC, 1991; pp 641–654.

- (115) Bobra, M. Water-in-oil emulsification: a physicochemical study. In *International Oil Spill Conference Proceedings*; American Petroleum Institute: Washington, DC, 1991; pp 483–488.
- (116) Strøm-Kristiansen, T.; Lewis, A.; Daling, P. S.; Hokstad, J. N.; Singaas, I. Weathering and dispersion of naphthenic, asphaltenic, and waxy crude oils. In *International Oil Spill Conference Proceedings*; American Petroleum Institute: Washington, DC, 1997; pp 631–636.
- (117) Lessard, R. R.; DeMarco, G. The significance of oil spill dispersants. *Spill Sci. Technol. Bull.* **2000**, *6*, 59–68.
- (118) Thingstad, T.; Pengerud, B. The formation of “chocolate mousse” from Statfjord crude oil and seawater. *Mar. Pollut. Bull.* **1983**, *14*, 214–216.
- (119) Daling, P. S.; Leirvik, F.; Almås, I. K.; Brandvik, P. J.; Hansen, B. H.; Lewis, A.; Reed, M. Surface weathering and dispersibility of MC252 crude oil. *Mar. Pollut. Bull.* **2014**, *87*, 300–310.
- (120) Gros, J.; Nabi, D.; Würz, B.; Wick, L. Y.; Brussaard, C. P. D.; Huisman, J.; van der Meer, J. R.; Reddy, C. M.; Arey, J. S. First day of an oil spill on the open sea: early mass transfers of hydrocarbons to air and water. *Environ. Sci. Technol.* **2014**, *48*, 9400–9411.
- (121) Goldstein, B. D.; Osofsky, H. J.; Lichtveld, M. Y. The Gulf oil spill. *N. Engl. J. Med.* **2011**, *364*, 1334–1348.
- (122) Atkinson, R.; Arey, J. Atmospheric degradation of volatile organic compounds. *Chem. Rev.* **2003**, *103*, 4605–4638.
- (123) Deguillaume, L.; Leriche, M.; Amato, P.; Ariya, P. A.; Delort, A. M.; Pöschl, U.; Chaumerliac, N.; Bauer, H.; Flossmann, A. I.; Morris, C. E. Microbiology and atmospheric processes: chemical interactions of primary biological aerosols. *Biogeosciences* **2008**, *5*, 841–870.
- (124) Colcomb, K.; Bedborough, D.; Lunel, T.; Swannell, R.; Wood, P.; Rusin, J.; Bailey, N.; Halliwell, C.; Davies, L.; Sommerville, M.; Dobie, A.; Mitchell, D.; McDonagh, M.; Lee, K.; Shimwell, S.; Davies, B.; Harries, D. Shoreline cleanup and waste disposal issues during the Sea Empress incident. In *International Oil Spill Conference Proceedings*; American Petroleum Institute: Washington, DC, 1997; pp 195–198.
- (125) Michel, J.; Owens, E. H.; Zengel, S.; Graham, A.; Nixon, Z.; Allard, T.; Holton, W.; Reimer, P. D.; Lamarche, A.; White, M.; Rutherford, N.; Childs, C.; Mauseth, G.; Challenger, G.; Taylor, E. Extent and degree of shoreline oiling: Deepwater Horizon oil spill, Gulf of Mexico, USA. *PLoS One* **2013**, *8*, e65087.
- (126) Wang, Z.; Fingas, M.; Owens, E. H.; Sigouin, L.; Brown, C. E. Long-term fate and persistence of the spilled Metula oil in a marine salt marsh environment: degradation of petroleum biomarkers. *J. Chromatogr. A* **2001**, *926*, 275–290.
- (127) Owens, E. H.; Taylor, E.; Humphrey, B. The persistence and character of stranded oil on coarse-sediment beaches. *Mar. Pollut. Bull.* **2008**, *56*, 14–26.
- (128) Defeo, O.; McLachlan, A.; Schoeman, D. S.; Schlacher, T. A.; Dugan, J.; Jones, A.; Lastra, M.; Scapini, F. Threats to sandy beach ecosystems: a review. *Estuarine, Coastal Shelf Sci.* **2009**, *81*, 1–12.
- (129) Burns, K. A.; Garrity, S. D.; Levings, S. C. How many years until mangrove ecosystems recover from catastrophic oil spills? *Mar. Pollut. Bull.* **1993**, *6*, 239–248.
- (130) Mendelssohn, I. A.; Andersen, G. L.; Baltz, D. M.; Caffey, R. H.; Carman, K. R.; Fleeger, J. W.; Joye, S. B.; Lin, Q.; Maltby, E.; Overton, E. B.; Rozas, L. P. Oil impacts on coastal wetlands: implications for the Mississippi River Delta ecosystem after the Deepwater Horizon oil spill. *BioScience* **2012**, *62*, 562–574.
- (131) Michel, J.; Rutherford, N. Impacts, recovery rates, and treatment options for spilled oil in marshes. *Mar. Pollut. Bull.* **2014**, *82*, 19–25.
- (132) Bernabeu, A. M.; Nuez de la Fuente, M.; Rey, D.; Rubio, B.; Vilas, F.; Medina, R.; González, M. E. Beach morphodynamics forcements in oiled shorelines: coupled physical and chemical processes during and after fuel burial. *Mar. Pollut. Bull.* **2006**, *52*, 1156–1168.
- (133) Pineda-Flores, G.; Boll-Argüello, G.; Lira-Galeana, C.; Mesta-Howard, A. M. A microbial consortium isolated from a crude oil sample that uses asphaltenes as a carbon and energy source. *Biodegradation* **2004**, *15*, 145–151.
- (134) Tavassoli, T.; Mousavi, S. M.; Shojaosadati, S. A.; Salehizadeh, H. Asphaltene biodegradation using microorganisms isolated from oil samples. *Fuel* **2012**, *93*, 142–148.
- (135) Hayes, M. H. B. Solvent systems for the isolation of organic components from soils. *Soil Sci. Soc. Am. J.* **2006**, *70*, 986–994.
- (136) Michaels, D.; Howard, J. Review of the OSHA-NIOSH response to the Deepwater Horizon oil spill: protecting the health and safety of cleanup workers. *PLoS Curr.* **2012**, *4*, e4fa83b7576b6e.
- (137) Schwarz, J. R.; Walker, J. D.; Colwell, R. R. Deep-sea bacteria: growth and utilization of hydrocarbons at ambient and in situ pressure. *Appl. Microbiol.* **1974**, *28*, 982–986.
- (138) Kimes, N. E.; Callaghan, A. V.; Aktas, D. F.; Smith, W. L.; Sunner, J.; Golding, B. T.; Drozdowska, M.; Hazen, T. C.; Suflita, J. M.; Morris, P. J. Metagenomic analysis and metabolite profiling of deep-sea sediments from the Gulf of Mexico following the Deepwater Horizon oil spill. *Front. Microbiol.* **2013**, *4*, 50.
- (139) Van Hamme, J. D.; Ward, O. P. Influence of chemical surfactants on the biodegradation of crude oil by a mixed bacterial culture. *Can. J. Microbiol.* **1999**, *45*, 130–137.
- (140) Lindstrom, J. E.; Braddock, J. F. Biodegradation of petroleum hydrocarbons at low temperature in the presence of the dispersant COREXIT 9500. *Mar. Pollut. Bull.* **2002**, *44*, 739–747.
- (141) Venosa, A. D.; Holder, E. L. Biodegradability of dispersed crude oil at two different temperatures. *Mar. Pollut. Bull.* **2007**, *54*, 545–553.
- (142) Hamdan, L. J.; Fulmer, P. A. Effects of COREXIT® EC9500A on bacteria from a beach oiled by the Deepwater Horizon spill. *Aquat. Microb. Ecol.* **2011**, *63*, 101–109.
- (143) Urbanczyk, H.; Ast, J. C.; Higgins, M. J.; Carson, J.; Dunlap, P. V. Reclassification of *Vibrio fischeri*, *Vibrio logei*, *Vibrio salmonicida* and *Vibrio wodanis* as *Aliivibrio fischeri* gen. nov., comb. nov., *Aliivibrio logei* comb. nov., *Aliivibrio salmonicida* comb. nov. and *Aliivibrio wodanis* comb. nov. *Int. J. Syst. Evol. Microbiol.* **2007**, *57*, 2823–2829.
- (144) Fuller, C.; Bonner, J.; Page, C.; Ernest, A.; McDonald, T.; McDonald, S. Comparative toxicity of oil, dispersant, and oil plus dispersant to several marine species. *Environ. Toxicol. Chem.* **2004**, *23*, 2941–2949.
- (145) McManus, M. A.; Woodson, C. B. Plankton distribution and ocean dispersal. *J. Exp. Biol.* **2015**, *215*, 1008–1016.
- (146) Prairie, J. C.; Sutherland, K. R.; Nickols, K. J.; Kaltenberg, A. M. Biophysical interactions in the plankton: a cross-scale review. *Limnol. Oceanogr.* **2012**, *2*, 121–145.
- (147) Ottosen, E. A.; Young, C. R.; Eppley, J. M.; Ryan, J. P.; Chavez, F. P.; Scholin, C. A.; DeLong, E. F. Pattern and synchrony of gene expression among sympatric marine microbial populations. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, E488–E497.
- (148) *Dispersant Tools, Job Aids and Decision Process*; Region X Regional Response Team, 2015. www.rtt10nwac.com/Files/NWACP/2015/Section%209406.pdf.