

## Dispersants -The Good, the Bad and the Rise of a New Bio-Based Generation

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### Commentary

The Deepwater Horizon (DWH) disaster, which occurred on April 20<sup>th</sup> of 2010, is heralded as the largest oil spill in U.S. history, and one of the largest maritime spills on record for the oil and gas industry. Only the Ixtoc-I oil spill that occurred in the Bay of Campeche in 1979, also in the Gulf of Mexico, ranks in the same league. Now a major motion picture starring Mark Wahlberg, the film Deepwater Horizon captures the gruesome ordeal that over one hundred crew members faced in their battle to survive an inferno of sweltering heat and mayhem on the burning oil rig that resulted in the death of 11 crew members and injury to many others. Whilst there was catastrophic drama above water, below the cloak of the sea surface an estimated 4.9 million barrels (ca. 700,000 tonnes) of crude oil, and over 250,000 metric tonnes of natural gas, largely methane, gushed out of the leaky Macondo well into the Gulf of Mexico over a period of almost 3 months. Due to the magnitude of the spill, its duration, and the unprecedented response by combat teams, the DWH disaster remains the costliest oil spill in U.S. history, and resulted in environmental, social, and economic turmoil. Rarely has a human-made disaster ever stopped the clock on the research programmes of so many scientists in a nation, with scientists from universities and government-funded agencies all over the United States and in other countries placing a hold on their research programmes to turn their attention to the DWH spill. A recent survey analysing world-wide interest in research on marine oil spills reported that following the DWH oil spill, there has been an enormous shift in research focusing on the Gulf of Mexico - from 2% of studies in 2004-2008 to 61% in 2014-2015, and the spill appears likely responsible for doubling the proportion of studies that consider dispersants [1].

The spill produced new challenges and unexpected complications for oil-spill response and mitigation teams, as it was unprecedented on several counts. Firstly, the DWH exploratory well was the deepest the oil and gas industry had ever drilled in the ocean, marking it as an extraordinary engineering feat. Secondly,

the spill occurred at a depth of about 1.5 km below the sea surface, so is the deepest accidental oil spill in the history of the industry. Thirdly, because it occurred in deep water, an unprecedented oil plume formed in the subsurface (at 1100-1300 m depth), making it difficult to track, monitor and, thus, assess its fate and impact to subsurface and benthic systems. The area covered by the spill on the sea surface in the Gulf was, in itself, roughly equivalent to the size of the state of Virginia. Now, just over six years on, the full environmental impact of DWH remains unresolved. Research on several fronts still continues today on the spill, one of which relates to the use of dispersants with respect to their effectiveness balanced against toxicology to marine organisms and their influence on the activities of microbial communities responsible for degrading the hydrocarbons that constitute crude oil.

Dispersants include surfactants that have the effect of breaking up the oil into smaller droplets so that they are more likely to disperse/dissolve into the water column. Using dispersants has three main benefits as a contingency response tool for combating oil spills. Firstly, they increase the dispersion of the oil in the water column, which means less oil will reach shorelines and fragile environments. Secondly, birds and other animals that abound and frequent on the sea surface will likely encounter less oil. Thirdly, dispersants are supposed to enhance the rate of oil biodegradation by hydrocarbon-degrading microorganisms. This last point has important consequences to the fate of the oil in the marine environment. By enhancing the amount of oil that physically mixes in the water, dispersants effectively make the oil more accessible (i.e. bioavailable) to microorganisms for biodegradation. Microorganisms, principally hydrocarbon-degrading bacteria, play a fundamental role in the degradation of oil, which will occur only if the hydrocarbon molecules (the constituents of oil) become dissolved in the water. Degradation can also occur at the oil-water droplet interface and the smaller the oil droplet size, the greater the oil surface area available for hydrocarbon-degrading bacteria to latch on to the droplet surface and degrade the oil. But how dispersants

behave, and whether they promote the oil biodegradation process, does not always follow suit.

At the direction of the Federal On-Scene Coordinator, responders to the DWH spill commenced spraying dispersants on sea surface oil slicks by April 22 (within 48 hours of the blowout), and on May 10 the EPA adopted a testing protocol created by NOAA and BP scientists for subsea dispersant use. Unprecedented quantities, up to seven million liters, of the dispersant Corexit EC9500A was applied by spraying on sea surface oil slicks and subsequently directly injected at the leaky wellhead near the seafloor (National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling, 2011) [2]; this was after the dispersant Corexit 9527 was used initially. This subsurface injection of Corexit resulted in droplet size distributions of approximately 10  $\mu\text{m}$  to 30  $\mu\text{m}$  in diameter in the deep-water oil plume, which significantly facilitated biodegradation. The smaller-sized oil droplets resulted in faster degradation by microorganisms, with almost 100% degradation of low- and medium-molecular weight Polycyclic Aromatic Hydrocarbons (PAHs) after 16 days, compared to 89% degradation of the larger-sized oil droplets [3]. Other studies, however, showed that the application of Corexit inhibited the natural enrichment of some major oil-degrading bacteria, such as *Rhodococcus* [4], *Marinobacter* [5] and *Acinetobacter* [5]. It has been posited that this inhibitory effect could be due to: 1) a chemical component(s) of the Corexit formulation, such as organic sulfonic acid salt, propylene glycol (solvent) and/or the surfactant chemical itself, Dioctyl Sulfo succinate (DOSS), 2) an increase in the soluble concentration of toxic hydrocarbon compounds due to the presence of the dispersant, and/or 3) competition by other oil-degrading bacteria that are more resilient in the presence of the dispersant. Whilst studies assessing the effect of the dispersant on the microbial response and degradation of the oil have employed state-of-the-art analytical and sequencing techniques (e.g. Kleindienst et al., 2015b; see references in Kleindienst et al., 2015a) [6,7], these studies are unfortunately few and far between. More research is needed to better understand the effects of dispersants on the microbial response and how it evolves and influences the oil biodegradation process using advanced sequencing technologies, bioinformatics and chemical analyses. Such studies should be done, if at all possible, under conditions that simulate those *in situ*.

Chemical dispersants have been used for over 50 years and are the preferable treatment for marine oil spills. In the U.K., dispersants have been used since 1967 when the first major oil spill, the Torrey Canyon, released up to 50,000 tons of crude near the coast of Cornwall. Approximately 13,500 tons of a dispersant agent, which consisted of more than 60% aromatic solvents, was used to clean up the oil [8]. Since then, a newer generation of less toxic and more efficient chemical dispersants was developed, of which Corexit is the most widely used. But is this enough to satisfy concerns on their use considering the massive quantities that are released at sea to treat large oil spills? Many hard lessons have been learned from the DWH spill, one of which has spurred inter-

est to search for alternative types of dispersants that have greater environmental compatibility. The toxicity of dispersants to marine life has come a long way since the first studies back in the 1960s [9], but their use does not fail to raise controversy and debate, even today. Numerous studies considering dispersants have reported conflicting results about their toxicological effects, even when the same type of dispersant was used across different studies.

The very nature that they are manufactured by organo-chemical synthesis and are used in such massive quantities during a spill assumes they would be of concern to marine life, even synergistically with the oil. Some toxicologists have questioned the reliability and comparability of the testing methods used by manufacturers, and moreover the testing used is limited to acute (short-term) toxicity studies on one fish species and one shrimp species and does not account for possible persistence of the dispersant in the environment and its long-term effects. This is an area that needs more attention if dispersants are to gain confidence from the scientific community and wider public for their use. In the end, their benefits should outweigh any acute or lasting damage they could pose to marine life and human health. A recent study employing a physical model to predict the fate of oil when gushing out from a deep subsurface well showed that using dispersants increased the entrapment of volatile compounds in the deep sea, thereby mitigating the release of volatile toxic hydrocarbons (e.g. benzene) into the atmosphere [10]. Whilst this reduces the exposure levels of these types of oil-derived toxic compounds to humans, birds and other terrestrial animals, it assumes that the risks of using dispersants to life in the subsurface would be higher compared to when dispersants are not used. Nonetheless, more studies need to be done and methods revised that test a wider spectrum of marine organisms under standardized methods to evaluate the potential toxicology of dispersants. What are the levels of toxicity for different worldwide-approved dispersants? What organisms (humans and other life forms) are affected, and under what conditions? These are pertinent questions that are not, at present, sufficiently addressed under the current programme of required testing of dispersants, but which some academic research groups invest their time and funds to answering.

Corexit has become the most used dispersant worldwide, having been used in more than half of the major oil spills since the 1990s [11]. Like with all chemical dispersants that are stockpiled worldwide, the biodegradability of Corexit is not well understood. In order to be approved for use, all dispersant agents need to pass government-approved efficiency and toxicity tests [12]. Of the various worldwide-approved dispersants, most research has focused on their toxicity and long-term effects, whilst their biodegradability has received much less attention. In the case of Corexit, its biodegradability came to the attention of a few studies since the advent of the DWH spill. Its major surfactant component is DOSS, which was measured in the deep subsurface during the DWH spill at concentrations 36 times higher than in shallower waters, indicating that most of the DOSS was entrained in the deep

[13,14]. Conversely, in the warmer surface waters of the Gulf (25°C), DOSS biodegradation was significantly higher; implicating that temperature is an important factor that may dictate the residence time of the surfactant in the marine environment. The application of dispersants to treat oil spills is largely based on convenience and cost. Corexit, for example, is produced cheaply; it is stockpiled at quantities of many tonnes, and stands at the ready for use immediately in the event of a major spill. However, growing awareness among society regarding the health and environmental hazards associated with the use of chemical dispersants has led to increased preference towards the use of naturally-derived bio-based alternatives. Dispersants that contain surfactants derived from biological sources (aka bio-surfactants) are associated with having lower toxicity, higher biodegradability, and better environmental compatibility compared to their chemical counterparts that are produced from organo-chemical synthesis. Whilst they can be produced sustainably by fermentation using strains of bacteria or yeast, the high costs involved and the low yields that are often achieved are major factors that have precluded their penetration into the oil-spill dispersants market [15]. Culture medium alone, for example, can account for up to 50% of the overall production costs of bio-surfactants, therefore the replacement of expensive synthetic media by cheaper substrates derived from agro-industrial waste, for instance, is a possible cost-reducing measure [15]. Bio-surfactant production could also be enhanced at the industrial scale by employing highly-active bio-surfactant-producing bacterial strains (e.g. by genetic modification), and by optimization of the production and downstream recovery process [15].

The development of a new generation of dispersants that are as, or more, effective to commercial synthetic dispersants, cost efficient, and have minimal side effects when they come in contact with, or are ingested by, marine organisms and humans is a path that has gained traction since the DWH spill. Through the Gulf of Mexico Research Initiative (Go MRI) in the U.S., a number of projects are now underway aiming to develop bio-based dispersants using food-grade ingredients (e.g. silica, polyethylene glycol) that are common additives in food and medicine, and then can be obtained relatively cheaply by the tonne.

Lecithin in combination with Tween 80, which are both food-grade emulsifiers, have been shown to disperse and produce more stable emulsions of crude oil than Corexit [16]. The development of bio-based dispersants, such as those produced by microorganisms, could also be a major step forward to implementing a more environmentally compatible dispersant product for combating oil spills. To realize this, there is an urgent need to overcome some major limitations surrounding the microbial production of bio-surfactants, principally the high costs involved and the relatively low yields that are often achieved from microorganisms. In order to help overcome these limitations, the following areas should be explored: 1) The use of low-cost, alternative and sustainable substrates/feed stocks for bio-surfactant production in fermentation processes; 2) The implementation of low-cost methods

for the downstream extraction and purification of bio-surfactants; 3) Exploring genetic engineering approaches to improve rates and yields of bio-surfactant production; 4) Expand bio-prospecting studies, especially at underexploited or extreme environments, to identify novel microbial strains that produce elevated levels of powerful bio-surfactants. With respect to this latter point, research on well-known bio-surfactant-producing microorganisms appears to have reached a peak, so the discovery of new bio-surfactant-producing microorganisms is an avenue that could hold a lot of promise in this respect. Nonetheless, however, there are still a number of loopholes and hurdles to traverse before a new bio-dispersant candidate reaches approval to be stockpiled and stand at the ready for use in the event of a spill; many of these relate to testing and approval by the Oil & Gas industry and international oil spill response authorities like OSRL (Oil Spill Response Limited). For a new generation of bio-dispersant agents to be realized, this effort will require a close engagement between the industry and academic research groups that are working on this.

Where dispersants are the first line of choice for treating an oil spill, it would seem logical to select the most suitable dispersant that will have the greatest effect in enhancing the microbial response – specifically of the oil-degrading bacterial population as these are the organisms that are pivotal in the biodegradation of the oil. Considering the millions of liters of oil that enters the marine environment every year from natural and anthropogenic sources, this oil volume is enough to cover the global oceans and seas by a few hydrocarbon molecules thick if it were not for the presence of these types of microbes. There is no warning when and where an oil spill will occur, so oil-spill response authorities are always at the ready to tackle a spill at anytime, anywhere, and under almost any type of condition. Every spill will be somewhat different, from the geographical location it occurs, to the environmental conditions at the time and the very nature of the spill (e.g. shallow vs deep water).

We may have entered a new era in the development of a new generation of dispersants produced from biological sources (i.e. bio-dispersants). Whilst it may be many years before any are approved and become part of the stockpiled inventory of dispersant agents that stand at the ready for use in the event of an oil spill, the future may hold promise for battling spills with a more environmentally- 'Friendly' breed of dispersants. The recent emergence of heightened research on this front seems promising. Whilst prevention of oil spills in the first place will help to reduce the overall volume of dispersants released into the marine environment, more reliance on bio-based alternatives should help reduce the potential detrimental environmental impacts compared to when chemical dispersants are used. In particular, it will be important to select dispersants that speed up the rate and extent that spilled oil is biodegraded by oil-degrading populations of microorganisms. To this end, funding and collaborations between the Oil & Gas industry and academic researchers, both domestic and internationally, needs to be expanded. There will be many challenges along

the way, but at the very start of this journey there will need to be a requirement for close engagement, and a building of trust, between academics and the industry.

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