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Chemical Dispersants and Crude Oil - Efficacy and Toxicity

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This is a guest post by Dr. Stephen R. Humphrey, known on The Oil Drum as NatResDr. Steve Humphrey has been on the faculty of the University of Florida since 1971. Currently he is Director of The School of Natural Resources and Environment. He also was a member of the Florida Environmental Regulation Commission for 8 years.

One of the striking controversies about the massive BP Deepwater Horizon oil well blowout has been alarm raised about chemical dispersants used to hold spilled crude oil deep in the Gulf of Mexico. Prospects for oil's direct harm to the environment, the economy, and coastal society were immediately obvious. But why were people so concerned that dispersing the oil was bad—worse than allowing it to come onshore? Is this just a case of "out of sight, out of mind" to benefit the oil company, or are there larger benefits that reduce the harms to other interests?

Initial accounts were vague, so I decided to don my rubber Spock ears and survey the scientific literature—more information signal, less noise. What do we really know about the use of dispersants? What do they do? What benefits and problems do they bring? I was most interested in the efficacy of dispersants. I read scores of peer-reviewed scientific articles, and below I highlight a few of the most informative studies, providing enough detail that the technically-minded reader should be able to judge the content. I also provide notes on other important questions, such as whether dispersants are toxic on their own and whether they make crude oil more or less toxic than it otherwise would be. Further review of such questions is warranted, however.

Background

As background, here are two of the better press reports on using dispersants on the BP oil spill:

Researchers Worry About Oil Dispersants' Impacts, Too

Slick Solution: How Microbes Will Clean Up the Deepwater Horizon Oil Spill

Use of dispersants on the BP spill reportedly began on April 27, 2010, but Corexit 9527A use was soon discontinued in favor of Corexit 9500.

Substantial information about dispersant use on this oil spill is provided at the EPA website.

Simply put, the purpose of dispersant is to emulsify the oil, like bacon grease in soapy dishwater. In the case of oil released underwater, dispersant reduces the amount of oil surfacing, hence reducing danger and toxicity for the topside workers trying to repair the damaged well and contain the spill. It also increases surface area and time for oil-droplet exposure to microorganisms in the water column. The microbes digest the oil into simpler and much less harmful chemicals, much as happens with household sewage in a septic tank or wastewater treatment plant.

Efficacy of dispersants

Much is known about which organisms (the biotic components) are important hydrocarbon degraders in the environment, the metabolic degradation pathways (the process mechanisms), and the fate of hydrocarbons in the environment, both in the presence of oxygen and its absence, as recently reviewed by Head et al. (2009; citation below). More than 200 genera of bacteria, cyanobacteria, fungi, and algae are known to degrade or transform hydrocarbons, using them for energy and carbon. Oil-consuming bacteria include sulfate-reducers and acid-producers, which thrive in anaerobic waters, whereas general aerobic bacteria require oxygen. Thus dissolved oxygen is not necessarily limiting to marine oil degradation (but low sulfate availability could be limiting in some situations). More generally, oil degradation in marine waters is strictly limited by the availability of nitrogen and phosphorus, and it also may be limited by bioavailability of the oil, as in cases of burial by mud or beach sand. Oil degradation is also temperature-dependent, but like surface waters, extreme marine environments (such as deep, dark, cold, high-pressure waters) also are occupied by diverse locally-adapted micro-organisms, including oil degraders (Margesin and Schinner. 2001. Biodegradation and bioremediation of hydrocarbons in extreme environments. Applied Microbiology and Biotechnology 56:650-663).

Crude oil is complex stuff, with four operationally defined groups of chemicals: saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes. Light crude is typically higher in the first two (lighter) groups than the last two heavy (polar) ones. At the marine surface, physical reduction (via evaporation and photo-oxidation) and biodegradation of light crude greatly reduces the proportion of the lighter fractions and increases the proportion of the heavier fractions. In deeper, dark waters, biodegradation proceeds without the benefit of the physical processes. In either place, degradation of the most voluminous fraction (saturated hydrocarbons) is prominent in reducing the volume of a spill, but the aromatic and heavy fractions are more toxic and persistent, so their fate is also quite important.

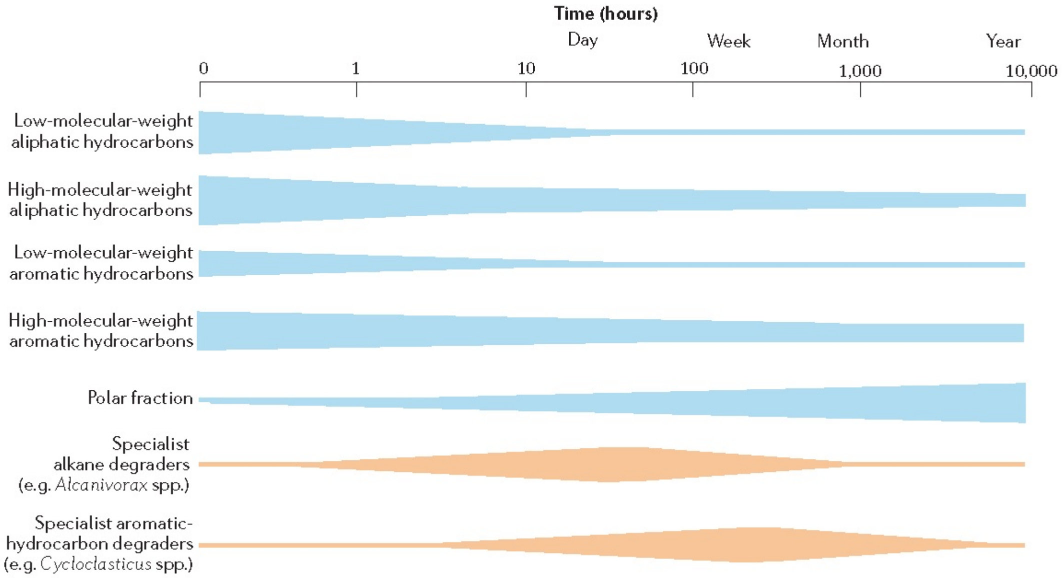


Figure 3 | **Changes in the composition of spilled oil and corresponding changes in the abundance of key organisms.** This schematic diagram represents general changes that have been observed in several studies. Slight variations are likely, both in the specific organisms that are involved and in the extent of biodegradation of different crude oils, which have a range of physical and chemical properties that affect their fate in the environment.

Head, Jones, and Röling. 2006. Marine microorganisms make a meal of oil. Nature Reviews Microbiology 4:173-182.

Normally the hydrocarbon-degrading organisms are diverse and widespread but not common in the environment. When crude oil is introduced, however, these organisms are favored by the new conditions, and their populations bloom and become very abundant in a short time. Some of these organisms consume mainly saturated hydrocarbons, while others consume mainly aromatic hydrocarbons, and these fractions can be largely removed within a few weeks by biodegradation.

Lessons learned about biodegradation and remediation of oil spills have come mainly from beach sites and laboratory microcosm studies; much less is known about the course of open-ocean spills, whether treated or not. Both beach and ocean surfaces can be treated with dispersants and or fertilizers, but deepwater environments can be treated only if injection at the oil source is an option. Note that such deepwater injection, if overdone, would cause undesirable pollution in its own right. In microcosms, Röling et al. (2002) showed that the amount of oil degradation is strongly related to the amount of nitrogen and phosphorus available. With no fertilizer added, oil degraded quite slowly, but small amounts of nutrients were introduced by death of the microbial biomass, suggesting that a self-reinforcing process operates, albeit modestly. Oil degradation in fertilized microcosms proceeded more rapidly when more nutrients were provided, but the final extent was similar if enough time passed. Managed addition of particular oil-degrading organisms has often failed to improve biodegradation, either because factors other than the presence of particular organisms is important or because the organisms added are poorly adapted to the field environment and thus have poor survival.

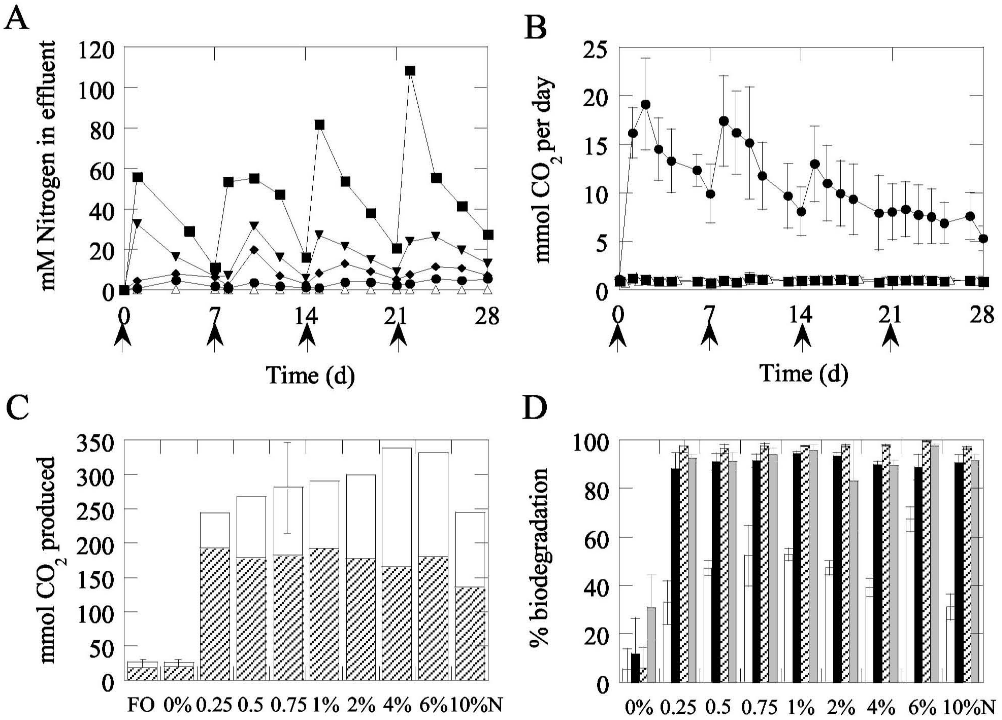


FIG. 2. Chemical data from microcosms. (A) amounts of nitrogen in residing seawater of beach microcosms over time. Symbols: △, 0% N; ●, 1% N; ♦, 2% N; ▼, 4% N; ■, 10% N. Arrows indicate addition of nutrients. (B) Daily carbon dioxide production, averaged over three independent runs, with bars indicating standard deviation, for microcosms. Symbols: △, FO; ■, 0% N; ●, 0.75% N. For the FO and 0% N microcosms, standard deviation symbols were often smaller than the data symbols. Arrows indicate addition of nutrients. (C) Cumulative carbon dioxide production in microcosms. The open portion of the column indicates production during the first 7 days; carbon dioxide production during the last 21 days of the experiment is shown by the hatched portion of the column. Standard deviations are shown by error bars for the microcosms prepared in triplicate (FO, 0% N, and 0.75% N). (D) Percentage of biodegradation of TPH (open), TRH (black), *n*11-to-*n*33 alkanes (hatched), and PAH (grey) per treatment. Error bars indicate standard deviations.

Röling, et al. 2002. Robust hydrocarbon degradation and dynamics of bacterial communities during nutrient-enhanced oil spill bioremediation. Applied Environmental Microbiology 68:5537-5548.

Venosa and Holder (2007) measured biodegradation of the highly bio-available fractions of dispersed crude oil, using Corexit 9500 and JD2000 in laboratory flasks that were constantly shaken. The rate of degradation was strongly temperature-dependent because of lower bacterial metabolic rates at lower temperatures. Degradation was much more rapid for dispersed oil than for non-dispersed oil, because in the non-dispersed control the microbial culture first had to generate its own biosurfactant to emulsify the oil before substantial degradation could occur. Eventually, however, the degradation of non-dispersed oil caught up with that of dispersed oil in terms of residual concentrations.

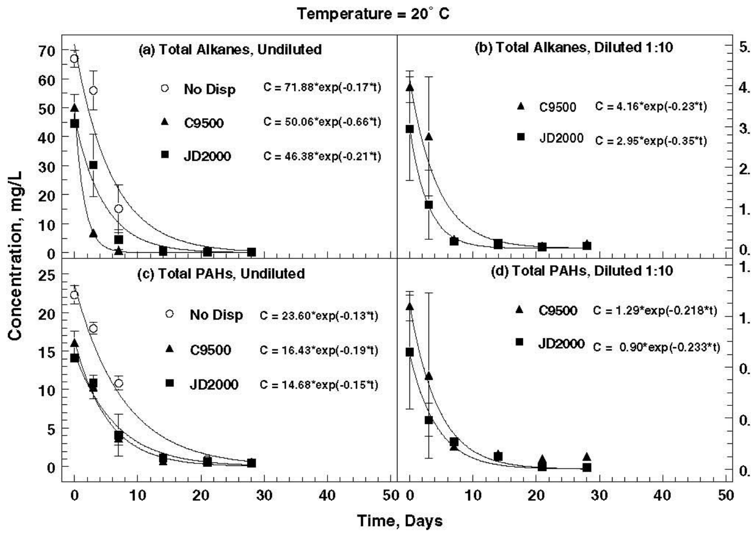


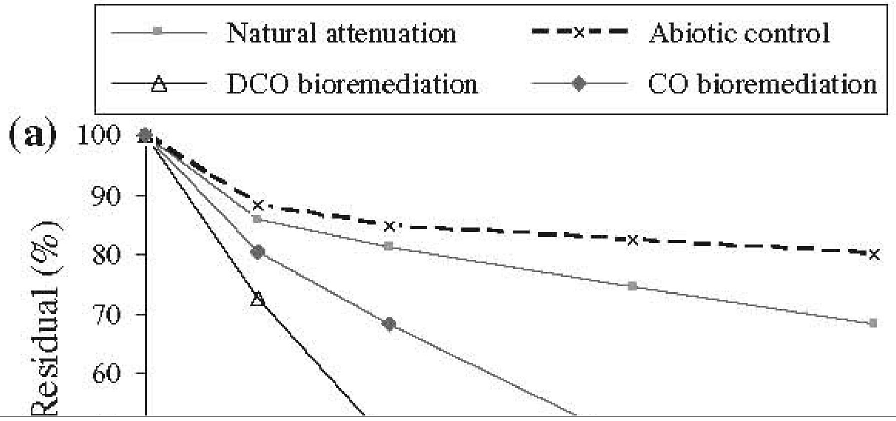
Fig. 1. Biodegradation of total alkanes and total aromatics in crude oil either non-dispersed or dispersed by Corexit 9500 and JD2000 undiluted (a and c) and diluted 1:10 (b and d). Temperature = 20 °C.

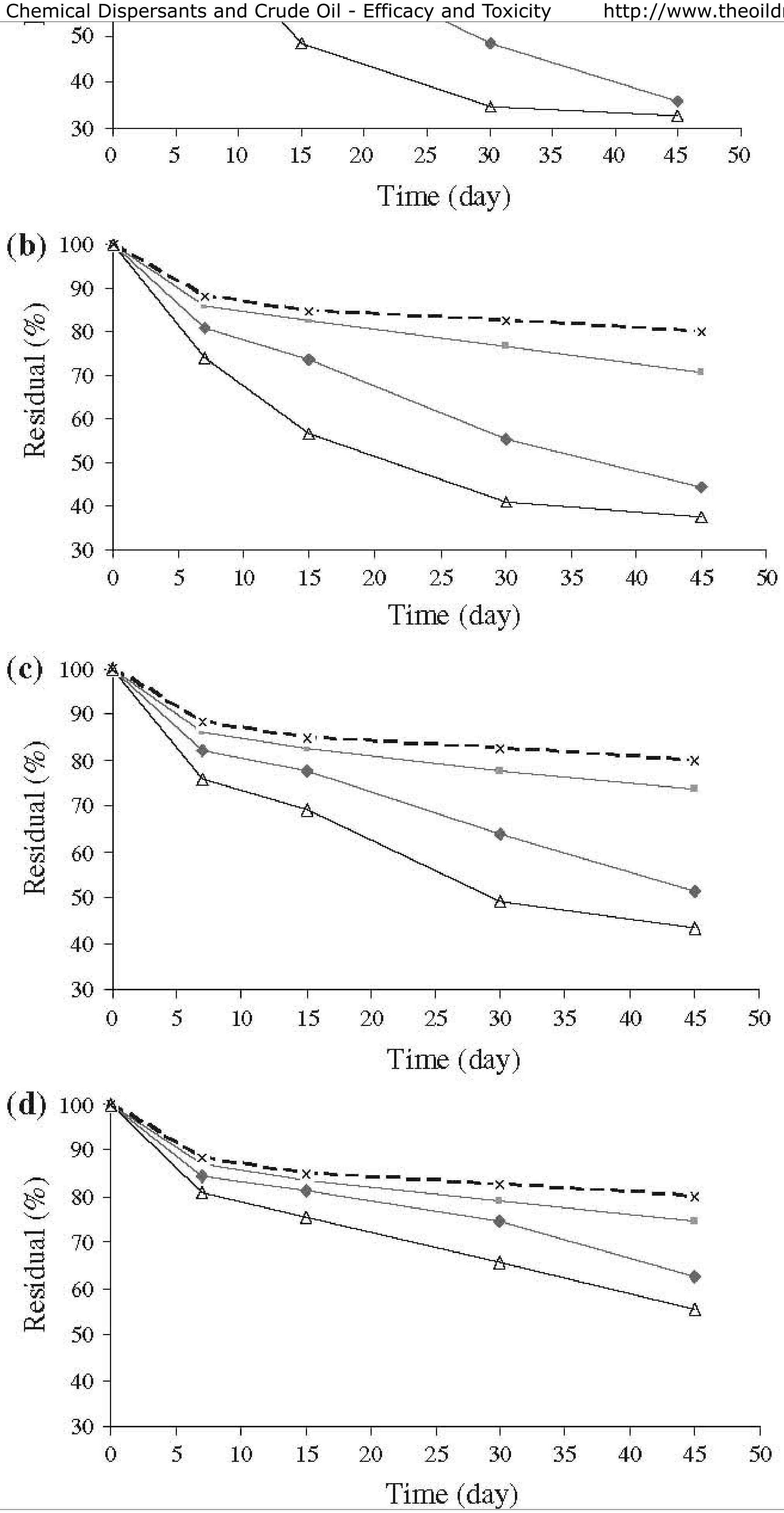
Venosa and Holder. 2007. Biodegradability of dispersed crude oil at two different temperatures. Marine Pollution Bulletin 54:545-553.

Zahed et al. (2010) studied biodegradation of light crude oil (the full complement of fractions) in seawater samples taken into the lab from coastal Malaysia (several sites to obtain representative biotic communities), using Corexit 9500 dispersant. They measured removal of total petroleum hydrocarbons over 45 days under several treatments, with initial oil concentrations of 100, 500, 1,000 and 2,000 mg/L. Treatments were

(1) seawater with locally acclimated microorganisms cultured in fertilizer (**CO**),
(2) seawater with microbes cultured in fertilizer plus Corexit 9500 dispersant (**DCO**),
(3) **natural attenuation** of oil in seawater with no culture, fertilizer, or dispersant, and
(4) **abiotic control** seawater, treated with biocide to show effects of purely physical reactions.

(There was no treatment that included dispersant without cultured organisms and fertilizer.) Abiotic oil loss (evaporation, photo-oxidation and other physical reactions in the absence of microbial activity) in this study was 20%. Natural attenuation resulted in 25-32% oil removal, with more removal occurring the lower the initial concentration. DCO oil loss ranged from 45 to 67%, again with more removal occurring the lower the initial concentration. CO oil loss ranged from 38 to 64%. Thus one-third to two-thirds of the oil was destroyed via biodegradation over the course of 6 weeks. The oil-loss timelines show that long exposure of the oil to biodegradation processes was needed to maximize benefits of the breakdown process.

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Time (day)
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0 5 10 15 20 25 30 35 40 45 50
Time (day)
(d)
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Residual (%)
0 5 10 15 20 25 30 35 40 45 50
Time (day)

Fig. 1 Reduction of oil concentration in bioreactors containing an initial oil concentration of **a** 100 mg/L, **b** 500 mg/L, **c** 1,000 mg/L and **d** 2,000 mg/L

Zahed et al. 2010. Effect of initial oil concentration and dispersant on crude oil biodegradation in contaminated seawater. Bulletin of Environmental Contamination and Toxicology 84:438-442.

Toxicity of dispersants

The US National Research Council issued a report on dispersants in 2005. The report succinctly noted the tradeoffs involved in dispersant use: "Dispersant application thus represents a conscious decision to increase the hydrocarbon load (resulting from a spill) on one component of the ecosystem (e.g., the water column) while reducing the load on another (e.g., coastal wetland). Decisions to use dispersants, therefore, involve trade-offs between decreasing the risk to water surface and shoreline habitats while increasing the potential risk to organisms in the water column and on the seafloor."

The report identified several critical knowledge gaps, including toxicity to particular organisms from exposure to dispersed oil, the final fate of chemically dispersed oil, and the effectiveness of dispersants for different oil types and environmental conditions. One key finding was: "The mechanisms of both acute and sublethal toxicity from exposure to dispersed oil are not sufficiently understood. Recent studies in the literature suggest that toxicity from physically and chemically dispersed oil appears to be primarily associated with the additive effects of various dissolved-phase polynuclear aromatic hydrocarbons (PAH) with additional contributions from heterocyclic (N, S, and O) containing polycyclic aromatic compounds. Additional toxicity may be coming from the particulate, or oil droplet, phase, but a particular concern stems from potential synergistic effects of exposure to dissolved components in combination with chemically dispersed oil droplets."

Based on that finding, the NRC report recommended that "Relevant state and federal agencies, industry, and appropriate international partners should develop and fund a series of focused toxicity studies to determine the mechanisms of both acute and sublethal toxicity to key organisms from exposure to dispersed oil."

However, relatively little subsequent progress has been made on the research agenda identified in the NRC report. A major reason that the body of research on dispersants is inconclusive (inconsistent among studies) is that disparate methodologies have been used.

In June 2010, the EPA reported toxicity tests of 8 dispersants (not combined with crude oil), including those being used in the BP spill. The dispersants were roughly similar to one another in toxicity when tested on the EPA-standard test organisms, mysid shrimp and silversides fish. The dispersants were also generally less toxic than oil, and they were expected to biodegrade in weeks or months rather than years as is the case for oil.

Fuller et al. (2004) applied standard EPA test protocols to mysid shrimp and silversides and sheepshead fish exposed to Arabian crude oil, Corexit 9500 dispersant, and oil plus dispersant. Oil plus dispersant was equal or less toxic than oil only. Continuous exposures were generally more toxic than declining exposures. Unweathered oil-only (dominated by soluble hydrocarbon fractions) were more toxic to silversides than weathered oil-only in which colloidal oil fractions dominated. Oil-plus dispersant media prepared with unweathered and weathered oil showed no difference in toxicity. The authors inferred that toxicity was a function of the soluble crude oil components and not the colloidal components.

Fuller et al. 2004. Comparative toxicity of oil, dispersant, and oil plus dispersant to several marine species. Environmental Toxicology and Chemistry 23:2941-2949.

Now the US EPA is testing the toxicity of Louisiana sweet crude oil combined with dispersant. These important results are expected by the end of July 2010.

A recent study indicates that dispersants alone are directly toxic to corals (Shafir, Rijn, and Rinkevich. 2007. Short and long term toxicity of crude oil and oil dispersants to two representative coral species. Environmental Science & Technology 41:5571-5574; Corexit was not tested in this study). Several coral reefs are in the vicinity of the BP oil slick, including the Flower Bank Gardens off the coast of Louisiana and Texas (designated as a marine sanctuary in 1992) and the Florida Middle Grounds, off the Florida panhandle. This issue may also be relevant to the Florida Keys, Yucatan, and Cuba.

Another issue worth watching is potential health problems for workers handling dispersant:

New BP Data Show 20% of Gulf Spill Responders Exposed to Chemical That Sickened *Valdez* Workers

New Data from BP's Coverup Firm Shows Dispersants in 20% of Offshore Workers

Final comments

Prolonging spilled crude oil's exposure to offshore sea life increases environmental harms in ways we don't understand very well, and these harms are probably much worse than we know. In my opinion there's no silver lining among the tradeoffs, only trading off one bad against other bads.

It's remarkable to me how much people have discussed toxicity of dispersants, and how little people have discussed the toxicity of crude oil, which is high for people and many other organisms. We definitely need to learn whether dispersant allows the oil to degrade fast enough and in large enough quantities to offset damage done by spreading the oil through more of the environment for longer. But we also need a comparable public discussion of the toxicity of the oil to people, to habitats and animals along the shore, and to the myriad creatures of the Gulf of Mexico.