

Dispersant Use White Paper:

Degradation of Dispersants and Dispersed Oil

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Introduction

The addition of chemical dispersants to crude oil on the sea surface enhances the formation of small oil droplets that become entrained in the water column. Many of these droplets are small enough to be neutrally bouyant, and therefore, advective forces dilute the plume and transport the droplets far from the site of the original spill. Furthermore, the formation of small oil droplets increases the surface area of the oil-water interface where microbial degradation of oil most rapidly occurs. In addition, small droplets enhance dissolution of soluble and semi-volatile compounds into surrounding waters, wherein biodegradation is carried out by aqueous phase microbes. Under these conditions, oil concentration is effectively reduced below toxicity threshold limits, and biodegradation becomes the most important process in reducing the total mass of petroleum hydrocarbons in the environment.

Biodegradation of Chemically Dispersed Oil

The effect of chemical dispersion on the biodegradation rate of petroleum hydrocarbons has been studied for several decades, and it is generally agreed that

chemically dispersed oil is biodegradable. However, the observed effects of chemical dispersants on the rate of oil biodegradation have varied significantly among studies.¹ Whereas some studies observed stimulation of biodegradation rates by the use of chemical dispersants,²⁻⁵ chemical dispersion inhibited the biodegradation rate or had no effect in other studies.⁶⁻⁸ The effect of chemical dispersion on the rate of oil biodegradation has been further complicated by substrate-dispersant interactions associated with differences in the experimental test conditions, which caused the biodegradation of individual hydrocarbons to be stimulated by some dispersants and inhibited by others.⁹⁻¹¹ As a result, it is difficult to predict the effect of dispersants on the biodegradation of specific hydrocarbons based on chemical class (e.g., aliphatic vs. aromatic).^{8,9} Similarly, the effects of specific dispersants on biodegradation cannot be predicted based on the chemical characteristics of the surfactants or the hydrophile-lipophile balance (HLB) of the mixture.^{10,11}

Predicting the rate of oil biodegradation in the environment based on the results of laboratory studies requires the use of scalable, quantitative biodegradation kinetics models.¹ To be predictive, scalable models must treat oil as droplets suspended in water rather than as homogenous solutions of hydrocarbons in water and must consider the growth of the organisms responsible for biodegradation. Unfortunately, only a few recent studies made any attempt to estimate biodegradation kinetic parameters,^{12,13} and those studies treated the oil as if it were a homogenous solution of dissolved components. They also neglected the concentrations of hydrocarbon-degrading bacteria, which may be one of the biggest differences between laboratory studies and the environment. Both studies estimated first-order (in oil concentration or the concentrations of specific oil

components) rate coefficients that were compared among treatments, but because only one independent rate coefficient was estimated for each treatment, treatment effects could not be rigorously evaluated. Zahed and colleagues observed consistent strong stimulation of the biodegradation rate of a mixture of light crudes (measured as total petroleum hydrocarbons) by addition of nutrients and a small additional increase due to chemical dispersion by Corexit 9500, but the rate and extent of oil biodegradation decreased as the oil concentration increased from 100 mg/L to 2000 mg/L.¹³ Venosa and Holder tested the effects of Corexit 9500 and JD2000 on the biodegradation rates of alkanes and PAH in Prudhoe Bay crude oil at two dispersed oil concentrations and two temperatures in nutrient-sufficient cultures.¹² The estimated first-order biodegradation rate coefficients were generally higher for dispersed oil than for undispersed oil, but the relative effects of the two dispersants varied with oil concentration and temperature. The biodegradation rates for alkanes and PAH were about 20%-80% lower at 5 °C than at 20 °C, but the effect of dispersed oil concentration was not systematic. Although experimental treatments were the same to provide comparative results on a relative basis, a confounding factor was the conduct of biodegradation experiments at 5 °C with dispersions produced at a higher temperature. The overall effect of temperature may be more complicated than that attributed to differences in first-order rate coefficients alone. The temperature at which the dispersion is made may affect the size distribution of the oil droplets that will influence mass transfer. However, since agitated conditions within a bottle minimize the effects of mass transfer on relative biodegradation rates, only a small increase in the rate of biodegradation with dispersant was observed in the lab experiments. This contrasts

with differences expected to occur in the open sea where agitation is much more gentle, causing mass transfer to govern biodegradation rates.

Biodegradation of Dispersants

Corexit 9500 and 9527 were the main dispersants used in response to the BP-*Deepwater Horizon* oil spill. The surfactants used in these two products are similar, including several nonionic compounds—sorbitan monooleate (Span 80), polyethoxylated sorbitan monooleate (Tween 80), and polyethoxylated sorbitan trioleate (Tween 85)—and the anionic surfactant diethylhexyl sulfosuccinate (DOSS),¹⁴ but the relative proportions of these compounds may differ somewhat between products.¹⁵ Detailed formulation and ingredient information on COREXIT dispersant products have been provided to the US EPA for its Gulf monitoring and environmental risk assessment program¹⁴. Essentially, the biodegradability of chemical constituents was a criterion in the selection of its ingredients by Nalco to minimize potential for risks to the environment or public health associated with its use.

Most studies on surfactant biodegradation, however, focus on surfactants that are used in high-volume consumer products, such as laundry detergents (e.g., linear alkyl sulfonates), or which have known environmental health and safety concerns (e.g., alkylphenol ethoxylates). For brevity, this section focuses on the fate of the surfactants used in the Corexit products that were used in the BP-*Deepwater Horizon* spill.

Biodegradation of oil-spill dispersants and the surfactants used in them has been studied for many years.^{8,16-20} Surfactant biodegradation studies usually distinguish

between primary biodegradation, which measures loss of surface activity,^{16, 17} and ultimate biodegradation, which also considers the removal of the intermediate products, usually based on oxygen consumption¹⁸ or carbon dioxide production^{8,17} relative to the amount expected based on the compound structure. Extensive, but incomplete, primary biodegradation of the ethoxylated nonionic surfactants used in Corexit 9527 and 9500, Tween 80 and Tween 85, was observed in pure cultures of marine bacteria isolated from an estuary in Spain.¹⁶ Primary biodegradation of Span 80, the unethoxylated nonionic surfactant used in both Corexit products, was less than 20% in the same study, but the authors suggested that the poor biodegradation may have been caused by substrate inhibition due to the extremely high surfactant concentration (5 g/liter), which likely would have impacted the integrity of bacterial membranes. Ultimate biodegradation of Tween 80 was about 50% in another study,¹⁹ and DOSS was extensively biodegraded by activated sludge bacteria,¹⁷ but the observed oxygen consumption or carbon dioxide production were much lower than expected for Corexit 9527¹⁸ and Corexit 9500,⁸ respectively, suggesting that biodegradation was incomplete. Some studies have suggested that partial biodegradation of Tween 80 involves metabolism of the oleic acid portion of the molecule, leaving the polyethoxy groups untouched or only partially metabolized.^{19,21} Note, however, that enzymatic oxidation and subsequent metabolism of polyethoxylate groups has been described.^{22,23}

These results suggest that the fate of dispersant surfactants is highly dependent on the concentration and chemical characteristics of the surface-active compounds, the microbes available, and the methods used to monitor biodegradability (as the separation of surfactants and the crude oil hydrocarbons remains a challenge in analytical

chemistry). Unfortunately, little information is available on the fate of surfactants in seawater at the concentrations that would be expected to result from dispersant use during spill response and in the presence of natural microbial communities, but one study conducted during the BP-*Deepwater Horizon* spill found no compelling evidence to support the hypothesis that DOSS biodegradation occurred in the deep hydrocarbon plume that originated at the wellhead.¹⁵ The study's authors concluded that although biodegradation may have occurred, dilution was probably the most significant factor contributing to a decrease in DOSS concentration at depth. Due to the level of uncertainty in the estimated DOSS release rate, the authors calculated that the biodegradation rate at the low 5 °C temperature at depth would have had to exceed the dilution rate by an order of magnitude to obtain statistically significant evidence for biodegradation of the surfactant.

Toxicity and Bioaccumulation of Dispersant Surfactants

The premise of dispersant use is based on the reduction of oil to concentrations below toxicity threshold limits. Based on recommended dispersant-to-oil (DOR) application rates, toxic effects are not considered a major factor at the concentrations encountered following their operational use. Thus, both Corexit 9527 and 9500 product formulations used in the Gulf of Mexico were approved by the EPA under the National Contingency Plan for the treatment of oil spills. In addition, a May 2010 report by the Centers for Disease Control concluded that “because of the strict guidelines that must be followed to utilize dispersants, it is unlikely that the general public will be exposed (directly) to (the) product.” The report further states that “ingredients are not considered

to cause chemical sensitization; the dispersants contain proven, biodegradable and low toxicity surfactants.”

In terms of potential environmental effects, while the focus of studies on chemically dispersed oil has been on the induction of acute and/or chronic toxic effects, some consideration has been given to the bioaccumulation of the surfactants. Uptake of two linear alkylbenzene sulfonates (LAS) by a freshwater oligochaete (*Lumbriculus variegatus*) and a larval insect (*Chironomus riparius*) was demonstrated using radioactive tracers, but the organic content of the test sediment was more highly linked to surfactant residue on the bodies of the test organisms than was the initial exposure concentration.²⁴ This study found that high organic content of the test sediment resulted in lower body residue concentrations, likely due to increased adsorption of the surfactant to the organic material contained in the sediment. This result is consistent with earlier research that concluded surfactants of all classes are readily taken up across the gills and that environmental variables can affect bioconcentration of surfactants.²⁵ Previous research also suggested that nonionic and anionic surfactants (such as those found in most oil dispersants) are biotransformed and eliminated via the gall bladder.²⁵

A review of the bioaccumulation potential of surfactants conducted by the European Oilfield Specialty Chemicals Association (EOSCA) found that although surfactants and their metabolites can be found in aquatic organisms following exposure, there is no evidence to support biomagnification of surfactants through the food chain.²⁶ The EOSCA report found that most of the available literature concerns a relatively small number of surfactant types and little attention has been given to long-term retention of surfactants accumulated within the bodies of exposed organisms. In fact, considerable

evidence suggests that surfactants are metabolized after uptake.^{26,27} Therefore, LAS, alcohol ethoxylates (AE), and structurally similar surfactants are unlikely to bioaccumulate to any significant degree.²⁷

Studies Conducted After the BP-Deepwater Horizon Oil Spill

Except for the study on DOSS fate described above,¹⁵ no studies conducted in conjunction with the BP-Deepwater Horizon oil spill specifically investigated the fate of chemically dispersed oil. Several studies, however, investigated the plume of dispersed oil and gas that extended southwest from the wellhead between about 1000 and 1200 m below the surface.²⁸⁻³² This plume was identified based on fluorescence,²⁸⁻³⁰ light scattering,²⁹ or the concentrations of specific hydrocarbons^{28,29,31,32} and was detectable up to 35 km from the MC252 wellhead.²⁸ The average temperature in the plume was about 5 °C.^{28,30} Most of these studies also observed a local dissolved oxygen (DO) minimum in the vicinity of the hydrocarbon plume. Camilli and colleagues attributed this minimum to hydrocarbon interference with the *in-situ* DO probes that were used because Winkler titration data did not show oxygen depletion within the plume.²⁸ Other studies, however, showed good agreement between data from the *in-situ* DO probe and Winkler titrations,^{31,32} suggesting that the rate of aerobic microbial metabolism within the plume was higher than in the surrounding water. Evidence supporting biodegradation of gaseous alkanes (e.g., methane, ethane, propane)^{31,32} and higher molecular weight normal alkanes³² was obtained based on compositional changes that reflected preferential utilization of specific compounds and (for ethane and propane) changes in $\delta^{13}\text{C}$.³¹ One

study estimated that about 70% of the oxygen depletion that was observed within the plume was due to microbial metabolism of ethane and propane.³¹ Microbial degradation of other hydrocarbons, including butane and longer chain alkanes, was responsible for the additional oxygen depletion. Hazen and colleagues estimated half-lives between about 1.2 and 6.1 days for higher molecular weight normal alkanes based on *in-situ* and microcosm data.²⁷ Because their biodegradation rate model did not include biomass concentration, however, and the *in-situ* half-lives did not consider dilution as a factor contributing to the observed changes in compound concentration, the similarity among the observed half-lives should not be over interpreted.

Flocs from samples collected within the plume between May 25 to June 2 were rich in microbes, oil, and oil degradation products, and bacterial counts were elevated within the plume.³⁰ Genes involved in hydrocarbon degradation were significantly increased ($p < 0.05$ or 0.01) in plume samples, and the relative abundance was correlated with the concentrations of some low molecular weight components of the oil, suggesting that the composition of the bacterial community changed in response to the presence of oil.³⁰ Cloning and sequencing of 16S rRNA genes showed that the relative abundance of 16 taxa of γ -Proteobacteria, including representatives of known psychrophilic and psychrotolerant hydrocarbon degraders, were higher inside the plume. The most abundant species in samples from within the plume (comprising about 90% of sequences) belonged to a single operational taxonomic unit that was closely related to *Oceanospirallaceae*.³⁰ Note that observations of samples collected in the same area by another research group about two weeks later, while oil was still being released from the wellhead, did not confirm high levels of *Oceanospirallaceae*, but the samples were

dominated by other putative hydrocarbon degraders, especially relatives of *Colwellia* and *Cycloclasticus*, which were thought to be growing on propane, ethane, and butane.³¹

The presence of the dispersants that were used was measured using indicator compounds, including 2-butoxyethanol, dipropylene glycol n-butyl ether (DPnB), propylene glycol, and DOSS. Except for offshore water column samples (79% positive), the dispersant indicators were observed in a small fraction (< 10%) of the samples that were tested. DPnB was the most commonly observed dispersant indicator compound, and its concentration decreased over time after dispersant application stopped in mid-July (Fig. 1).³³ The DPnB concentration was highest at the surface and subsurface between 1000 and 1400 m (Fig. 2). Deep water concentrations ranged from 0.0170 to 113.4 $\mu\text{g/L}$ with a mean of 4.3 $\mu\text{g/L}$.³³

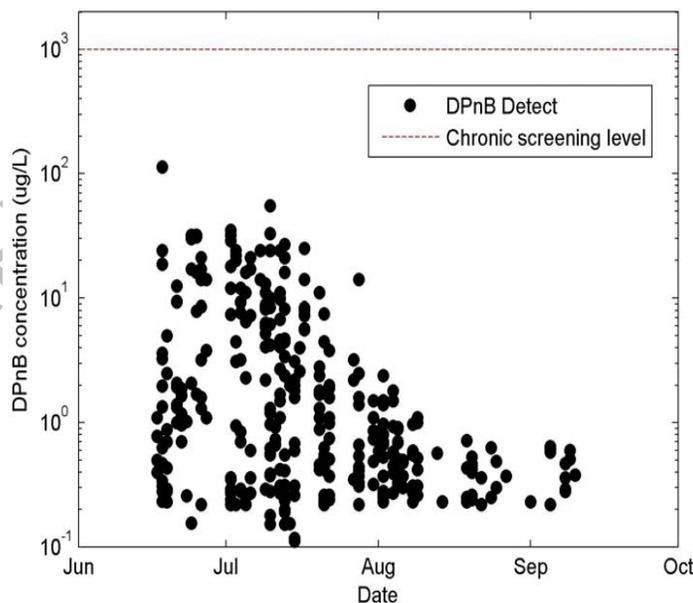


Figure 1: Offshore DPnB concentration over time; the United States Environmental Protection Agency benchmark (chronic screening level) is 1 mg/L. Figure from Ref. 33.

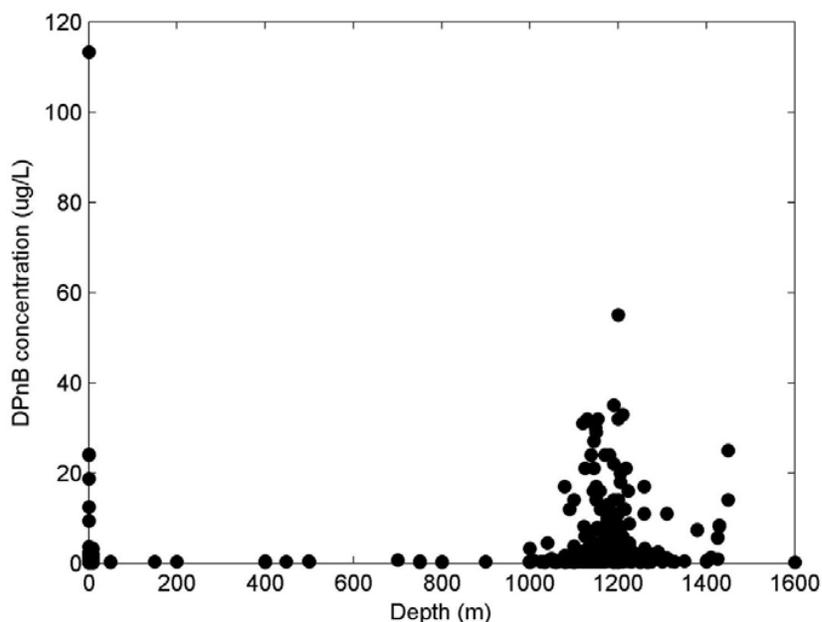


Figure 2: Concentration of DPnB with depth in water samples collected in the deep water zone of the Gulf of Mexico, defined as water depths of greater than 200 m. Figure from Ref. 33.

Conclusions

About 2.1 million gallons of dispersant were used during the BP-*Deepwater Horizon* spill response, and about 8% of the oil that was released is thought to have been chemically dispersed.³⁴ Based on current knowledge, there is no reason to believe that most of the chemically dispersed oil, including the MC252-derived hydrocarbons in the deep plume, will not biodegrade given sufficient time. Indirect evidence consistent with the expected biodegradation included identification of genes known to be involved in hydrocarbon biodegradation, enrichment of 16S rRNA sequences related to known hydrocarbon degraders, and depletion of dissolved oxygen within the deep dispersed oil plume. The estimated biodegradation rates for specific compounds are still open to debate due to

differences in experimental methodologies and the limited number of studies conducted to date. Unfortunately, scalable models to predict the fate of dispersed oil in the environment have not been fully developed or tested. Given the large uncertainties associated with measurements of hydrocarbon fate following accidental spills, fate and transport modeling may be the best tool available for evaluating the relative impacts and benefits of chemical dispersion in spill response.

In summary, due to the low concentrations of dispersant following its application in the Gulf of Mexico, as the result of physical dispersion and dilution processes, as well as the intrinsic levels of variability within an open-ocean environment, no evidence - direct or indirect - has been obtained to support the hypothesis that the dispersant surfactants biodegraded. However, in terms of environmental risk, it is important to note that all of the surfactants used in Corexit 9500 and Corexit 9527 are known to be at least partially biodegradable under appropriate conditions. Indeed, dispersants themselves can enhance the initial rate of petroleum hydrocarbon degradation by being the first substrate utilized by the hydrocarbon degrading bacteria to grow and colonize dispersed oil droplets.¹⁰

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