

Three Widely-Available Dispersants Substantially Increase the Biodegradation of otherwise Undispersed Oil

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Abstract

Dispersants are essential tools for responding to large marine oil spills, both at the surface and in deep water at uncontrolled well-heads. By reducing the interfacial tension between oil and water, they allow turbulence from surface wavelets or well-head ejection to disperse oil as tiny droplets (<70 μ m). Although the intrinsic density of the oil is unaffected, droplets are too small to rise rapidly, and minor turbulence and diffusive dilution impede droplet encounter and coalescence. Oil droplets disperse to very dilute concentrations, and provide substantial surface area for indigenous microbes to rapidly degrade the oil hydrocarbons. While the literature on this latter point is confused because few experiments have assessed biodegradation at environmentally relevant concentrations in natural seawater, we show here that three dispersants widely-available in international stockpiles effectively stimulate biodegradation when compared to oil in floating slicks, decreasing the residence time of the oil in the environment from many months (and potentially years if tarballs form or the oil reaches a shoreline) to a few weeks.

Keywords: Oil spills; Dispersant; Corexit 9500; Dasic Slickgone NS; Finasol OSR52

Introduction

Dispersants play a key role in oil spill response [1]. Although the preferred response is to collect spilled oil with booms and skim or burn it, large spills and/or bad weather can overwhelm even the largest booming operations. Dispersants then offer a bioremediation option for both surface and sub-sea releases, as demonstrated during the response to the Macondo Well blow-out in the Gulf of Mexico [2]. By decreasing the interfacial tension between oil and water, dispersants substantially decrease the amount of energy necessary to disperse oil as tiny droplets (<70 μ m) in the water column. Such droplets are essentially neutrally buoyant, so with minimal turbulence they stay in the water column and diffuse apart rather than coalesce and rise to the surface as a floating slick [3-7].

The tiny droplets of dispersed oil have long been thought to be ideal for microbial biodegradation because they are sufficiently dilute that the natural levels of oxygen, nitrogen, phosphorus and trace nutrients in the sea are unlikely to be substantially limiting [6-8]. Nevertheless the literature addressing this topic is confused, mainly because experiments have either been done at such high concentrations of oil that conditions are not relevant to an actual dispersed oil scenario [9-13], or at such low concentrations that the oil disperses regardless of dispersant addition [6,14,15].

We have developed a protocol that keeps undispersed oil floating as a slick in a small 'boom' for at least 60 days [16]. Here we assess whether three dispersants widely stockpiled around the world for emergency use [17] (Corexit 9500 [18], Finasol OSR52 [19] and Dasic Slickgone NS [20]) allow rapid and substantial biodegradation of the hydrocarbons of dispersed oil. We also test the inherent biodegradability of the dispersants in stringent, standardized tests [21]. This paper is an extended version of one presented at the Thirty-eighth AMOP Technical Seminar in 2015 [22].

Experimental Section

Seawater (salinity 30psu) was collected from the New Jersey (USA) shore on November 7, 2014, and aerated for 24 hrs at laboratory room

temperature (20°C) before assembling the experiments. Although the water temperature at the time of collection was 11°C, the experiments reported here were done at 20 \pm 2°C, which represents local water temperatures from July through September, under conditions of 16 hours of light, 8 hours of dark. The seawater contained no detectable hydrocarbons (<2 ppb), and acted as the source of oil- and dispersant-degrading microbes. The seawater was not filtered, and probably contained protists that may have consumed some of the bacteria during the incubations, as would occur at sea.

The ultimate biodegradability (complete mineralization) of the three dispersants, Corexit 9500, Slickgone NS and Finasol OSR 52 was followed in a multi-channel automated electrolytic respirometer (Coordinated Environmental Service, Ltd., Kent, England) at 20 \pm 2°C in agreement with the procedure outlined in the OECD 301 test guidelines [21]. The instrument uses sealed vessels, and as CO₂ is produced by the aerobic biodegradation of the substrate it is absorbed by a separate basic solution (2M NaOH). This reduces the ambient pressure in the vessel, and this is sensed by a sensitive pressure transducer that turns on the electrolysis of a copper sulfate solution until oxygen evolution restores the initial pressure. Thus although the vessels are sealed, the oxygen concentration remains constant throughout the experiment even though it is being consumed in the biodegradation.

Dispersant concentrations were tested at 5, 10 and 20 mg/L, all in triplicate, and the seawater was amended with 0.05% Bushnell Haas medium [23] to insure against nutrient limitation. Triplicate control samples, with the added nutrients but no added carbon source, served

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to monitor indigenous oxygen consumption, and this respiration was subtracted from all experimental data. The sodium benzoate control (50 ppm) degraded >60% by Day 12.

Oil biodegradation experiments followed the protocol outlined in [16]. Alaska North Slope crude oil was allowed to evaporate until it had lost 20% of its initial mass. This approximately mimics the evaporative loss likely to occur before dispersants might be deployed in a large offshore spill. Experimental vessels contained 4 L of seawater; for the undispersed oil incubations, 10 μ l of oil was placed inside a floating glass boom (enclosing a surface area of 28 mm², so the slick had a nominal thickness of 350 μ m, albeit with a meniscus around the edge). Other aliquots of the oil were pre-mixed with the respective dispersants at a dispersant: oil ratio of 1:20 and 10 μ l of the individual mixtures were added directly to 4 L of seawater with a positive-displacement pipette. All vessels were stirred with a 2 cm vortex. Experiments were done in duplicate, and experimental systems were sacrificed with exhaustive methylene chloride extraction after 7 and 62 days.

The methylene chloride extracts containing the extracted oil were concentrated to less than 1 mL, with care to not allow the evaporation to continue to dryness, and analyzed by GCMS using hopane as a conserved internal standard [24].

Results and Discussion

Mineralization of dispersants

The respirometer results indicated that approximately 32% of each of the three dispersants was mineralized in 28 days when tested at low concentrations (5-20 ppm) in natural seawater amended with trace nutrients – in general there was slightly more percent mineralization at the lower concentrations, but there were no statistically significant differences between either the different concentrations or the different dispersants. The 32% may be compared to 78% mineralization for the sodium benzoate positive control. All three dispersants are thus classified as inherently biodegradable in the OECD guidelines [21]. These results were expected, since many of the components of

dispersants are known to be biodegraded in seawater [25-27], and similar results were obtained with Corexit 9500 at -1°C [15].

Primary biodegradation of oil hydrocarbons

Figure 1 shows representative total ion chromatograms of the hydrocarbons of the initial oils, and oils extracted from experimental systems without or with the three dispersants investigated. Note the substantially more extensive biodegradation of the dispersed oil than of the floating slick, especially within the first 7 days of incubation. Although this is only a limited data set, it is clear that the data provide further confirmation of earlier work [6,14,16], where more accurate estimates of half-lives could be obtained. It is especially notable that the prominent *n*- and *iso*-alkanes (pristane and phytane) were consumed within a week in the dispersed samples, as was >90% of the phenanthrene and methylphenanthrenes (Figure 2). In contrast, only 70% of the phenanthrene, and 30% of the methylphenanthrenes were consumed from the slick after two months. Likely some of the losses of lighter components can be attributed to evaporation associated with undispersed oil at the water surface.

The extensive biodegradation of the alkylated phenanthrenes and chrysenes in the dispersed oil, but not the floating slick, is exhibited in Figures 3 and 4. As in previous experiments [14-16], there was no obvious preference for the biodegradation of individual isomers of the alkylphenanthrenes, but 3-methylchrysene was degraded more slowly than the other methylchrysenes. Benz[*a*]anthracene was degraded preferentially to chrysene (Figures 2 and 4).

Since the experiments reported here included only two timepoints (in duplicate) to assess biodegradation, we cannot reliably calculate half-lives for the individual hydrocarbons we have measured. Nevertheless the data are clearly consistent with the more extensive experiments reported elsewhere [14], which examined the biodegradation of oil dispersed with Corexit 9500. The half-life of total detectable hydrocarbons at this concentration (2.5 ppm oil) in unamended seawater with indigenous microbes is about a week, with half-lives for alkanes of a few days, and heavier aromatic components

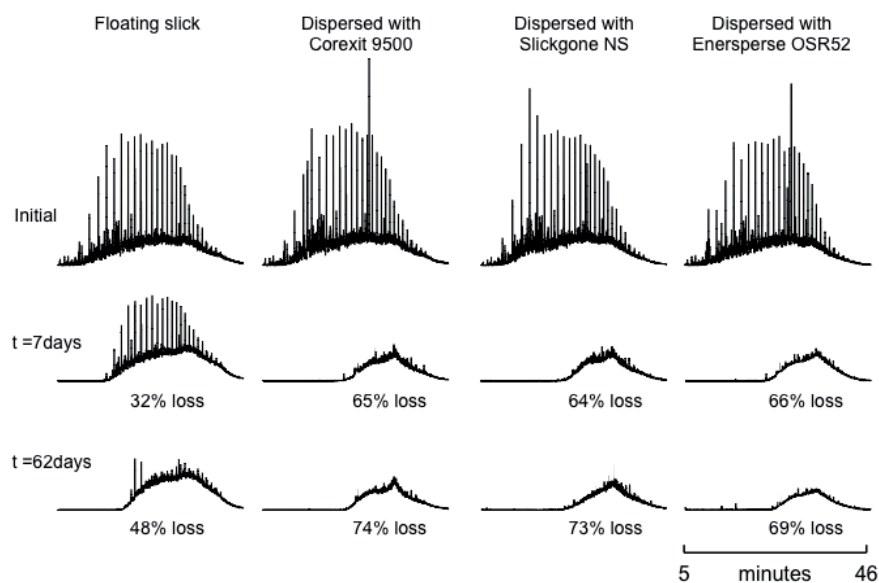


Figure 1: Total ion chromatograms of the initial oils used in the experiment, together with those extracted after 7 and 62 days of incubation at 20°C. These are representative chromatograms; each sample had a replicate. Chromatograms normalized to equivalent hopane.

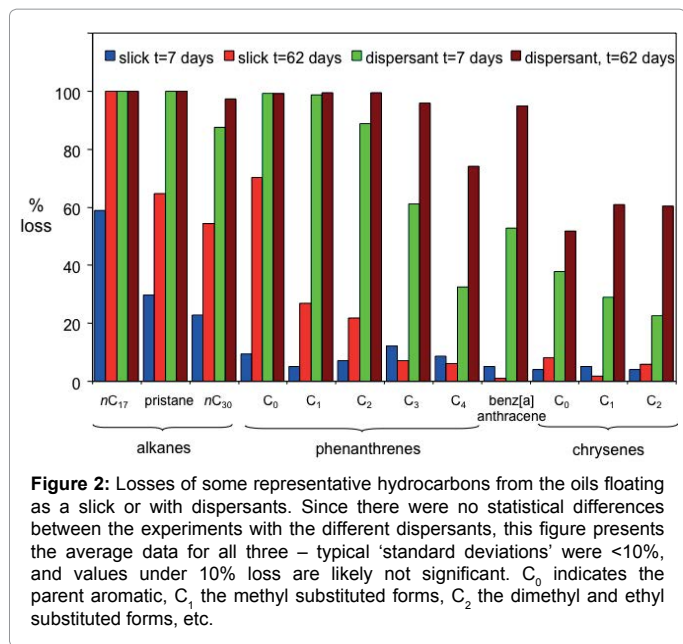


Figure 2: Losses of some representative hydrocarbons from the oils floating as a slick or with dispersants. Since there were no statistical differences between the experiments with the different dispersants, this figure presents the average data for all three – typical ‘standard deviations’ were <10%, and values under 10% loss are likely not significant. C₀ indicates the parent aromatic, C₁ the methyl substituted forms, C₂ the dimethyl and ethyl substituted forms, etc.

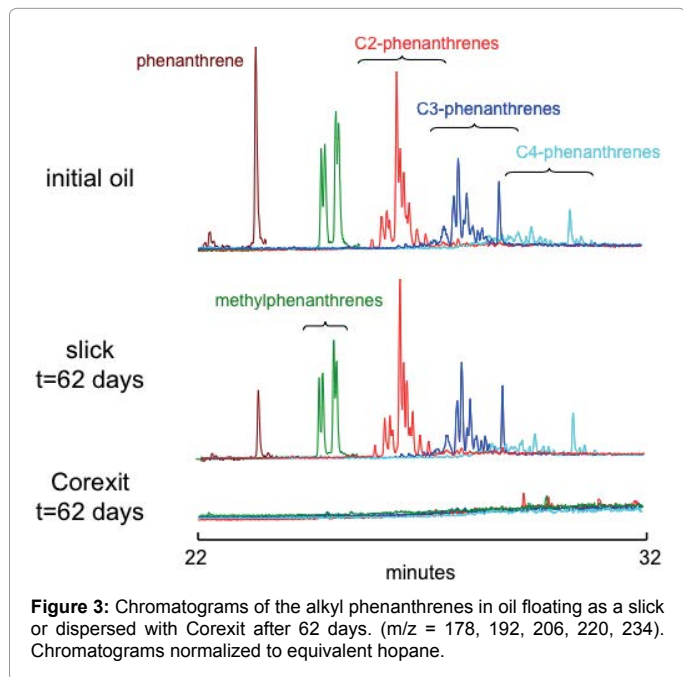


Figure 3: Chromatograms of the alkyl phenanthrenes in oil floating as a slick or dispersed with Corexit after 62 days. (m/z = 178, 192, 206, 220, 234). Chromatograms normalized to equivalent hopane.

such as chrysene having a half-life of about a month. We emphasize that the data from this study are fully consistent with other recently published work: similar values for alkanes of a few days were reported in the deep ‘plume’ from the Deepwater Horizon blowout [28], and in laboratory studies aiming to replicate field conditions [29]. Similarly rapid biodegradation of dispersed oil hydrocarbons was reported in Norwegian studies with controlled droplet sizes [6] and in flumes [30], and in an experiment carried out with rather higher oil concentrations and additional nutrients in water collected off the Penang, Malaysia, shore at 27.5°C [31]. All these studies used the indigenous microbes in the sea, and only the last added nutrients because rather high concentrations of oil were used (100 ppm oil). Concentrations of oil in dispersed slicks are much lower, typically <1 ppm [28,29,32-38]; we use

2.5ppm here because even that requires 4L of seawater to have enough oil for analysis, and we do not have facilities to run replicates of larger volumes.

Conclusions

The experiments reported here extend our previous work [14,16] with Corexit 9500 [18] to include Finasol OSR52 [19] and Dasic Slickgone NS [20]. All three dispersants are stored in large volumes around the world in case of need [17], and we show here that biodegradation of dispersed oil hydrocarbons with all three is indistinguishable. It is gradually becoming generally recognized that the role of dispersants is not to stimulate oil biodegradation *per se*; rather their role is to facilitate oil dispersion and reduce the potential for impacts to shorelines and critical in-shore natural resources [1]. Once oil is dispersed and allowed to diffuse to low concentrations so that individual droplets rarely have a chance to re-coalesce to floating slicks, biodegradation proceeds regardless of the presence of dispersants [14,15]. Indeed, in our experiments the few ppm of oil in stirred seawater would disperse irrespective of the presence of dispersant, unless the oil were to be corralled in a floating boom [16]. While there is uncertainty in quantitatively extrapolating such lab results to field conditions we can conclude that the three dispersants clearly do not inhibit biodegradation, contrary to what has been claimed in past work using unrealistic concentrations [9,39]. (While it is difficult to calculate the concentrations of oil used in the experiments of Kleindienst et al. [29], at most the inhibition they report is a factor of two, indicating that biodegradation is substantially faster than for an undispersed slick even under their experimental conditions). More reliable estimates of dispersant effectiveness at actually dispersing oil must come from large-scale tests at wave tanks such as Ohmsett [40]. Laboratory tests calibrated against such large-scale tests will also be useful [41].

Our experiments reinforce the conclusions [6,14-16,28-31] that effectively dispersed oil hydrocarbons have a notably short residence time in seawater – days to a few weeks for the different hydrocarbon components. This is in stark contrast to the fate of non-dispersed oil, which emulsifies and potentially persists for months to years, especially

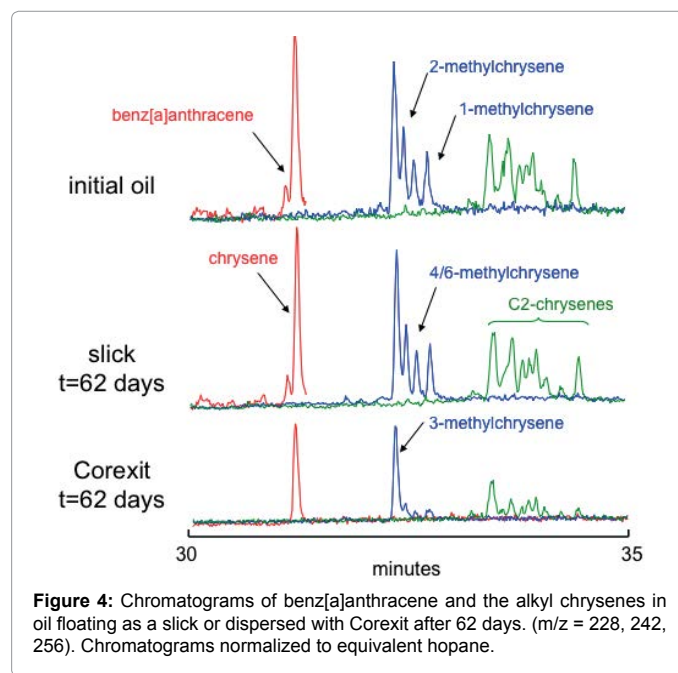


Figure 4: Chromatograms of benz[a]anthracene and the alkyl chrysenes in oil floating as a slick or dispersed with Corexit after 62 days. (m/z = 228, 242, 256). Chromatograms normalized to equivalent hopane.

if it reaches a shoreline [1]. This dramatically reduced residence in the environment effectively reduces longer-term oil exposures and potential for chronic impacts, and should be carefully considered when weighing the potential trade-offs of the use of dispersants in Net Environmental Benefit Analyses [42,43].

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