Coastal Response Research Center

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(APRIL 4 – MAY 4, 2016; 5:00 PM EASTERN TIME)

State-of-Science for Dispersant Use in Arctic Waters

Degradation and Fate

I. Fate of Dispersants

Knowns:

1. Specific components of dispersants have a longer half-life in the environment than other components.
   - Other sources of surfactants compound the problem of identifying dispersants used specifically in oil spill response.
2. Persistence of dispersant components is likely a function of environmental conditions. These conditions include:
   - Water column vs. sediments
   - Depth of water column
3. Anionic surfactants based on sulphosuccinates (e.g., DOSS dioctyl sodium sulfosuccinate) are biodegraded under aerobic conditions in water (Liu, 1983; Uña and García, 1983; Fraunhofer, 2003; García et al., 2009; Lee et al., 2011; Campo et al., 2013).
   - The studies cited just consider surfactants alone, not surfactants in a dispersant matrix except Campo et al. (2013), which deals with Corexit.
   - Hamden and Fulmer (2011) reported that hydrocarbon-degrading bacteria were inhibited by Corexit 9500, however, the concentrations of the dispersant used (10 to 100,000 mg/L) were much higher than those found in the environment during a spill.
4. In a recalcitrant matrix (e.g., asphaltenes, extremely weathered oil), these constituents may not be readily bioavailable for biodegradation by microorganisms (White et al., 2014).
5. Anionic branched alkyl sulphosuccinates have also been shown to biodegrade under anaerobic conditions, but at much slower rates than under aerobic conditions. Under anaerobic conditions, the linear sulphosuccinates degrade faster than the branched alkyl sulphosuccinates (García et al., 2009; Lee et al., 2011).
   - These data on biodegradation are just for surfactants, not surfactants in dispersant matrix.

6. As of 2014, the surfactant DOSS was detectible in low concentrations (from 22 to 3,700 nanograms per gram (ppb) dry sediment) in the Gulf of Mexico, in deep-sea sediments (<2 cm deep – White et al., 2012; Fisher et al., 2014) as well as in flocs on coral surfaces (White et al., 2014).
   - Kujawinski 2011 measured DOSS in a deep water plume in 2010 during DWH oil spill.
     - There is no evidence of long-term persistence (greater than 4 months) in water column.
   - In the studies cited above, DOSS was only found in DWH-oiled sediments.
     - Oiled sediments associated with natural seeps can have oil, but show no evidence of DOSS.
7. The behavior, fate, and degradation of DOSS are influenced by environmental factors and these same factors may have different effects on the fate of residual oil.
8. Sunlight exposure and oxidant production in the surface affect the fate of dispersant components (Glover et al., 2014; Kover et al., 2014).
9. Sunlight is poorly absorbed by the dispersant constituents.
   - Decay in sunlight can occur over a number of days.
   - Impact of temperature with respect to dispersant components is unknown; however, photodegradation of any compound is a function of the structure of that compound and, unless the structure undergoes temperature-dependent changes, the decay is independent of temperature.
10. Natural or anthropogenic organic matter, producing reactive oxygen species in conjunction with sunlight exposure, plays a role in the fate of dispersant components.
    - The organic matter can be generated by the oil that was spilled.
    - These processes are limited to the depth of water to which UV penetrates.
    - The characteristics of the background organic matter are important to understanding the pathway of degradation.
      - The implications for the Arctic (e.g., Chukchi vs. Beaufort Sea) are the variations in type and amount of NOM (natural organic matter), and seasonal variation of sunlight including presence of sea ice.
      - The interrelationships between these factors (sunlight, NOM (amount and type), oil (amount and type)) influence the amount of oxygenated species present to degrade constituents in dispersants.

Uncertainties:

1. Other sources of surfactants compound the problem of identifying dispersants used specifically in oil spill response.
   - It is unknown if this is an issue in the Arctic currently.

- Potential sources of surfactants such as urban discharges, etc. may be present in the Arctic.
- As of 2014, DOSS was detectible in low concentrations (up to 22 to 3,700 nanograms per gram dry sediment) in the Gulf of Mexico, in deep-sea sediments.
    - Background DOSS levels before DWH (or in Arctic) are unknown.
    - Data for one spill in Gulf of Mexico (DWH) – may not be applicable to others.

2. Decay of dispersants in sunlight can occur over a number of days.
    - Dispersant decay products are unknown.
    - Impact of temperature with respect to dispersant components is unknown.
3. The characteristics of the background organic matter are important to understanding the pathway of degradation.
    - The impact of this oxidation pathway has not been considered as a factor in biodegradation studies regarding dispersants.

II. Oil Sedimentation

The mechanisms for oil sedimentation are: oil-mineral aggregate (OMA)/oil-suspended particulate matter aggregation (OSA), bulk sinking and marine snow.

A. OMA/ OSA [natural material and drilling mud]*

*Information on the formation and transport of OMA/OSA is contained in the Physical Transport and Chemical Behavior document. This section focuses on the degradation and fate of OMA/OSA.

Knowns:

1. Fate and behavior of OMA formed is influenced by a number of environmental factors: oil, suspended material, water column depth, salinity, and mixing energy.
2. Weathering or biodegradation can cause increased OMA density, which can also cause sinking.

B. Bulk Sinking

Knowns:

1. Bulk sinking is defined as when the density of the oil mass increases over that of the surrounding water (e.g., residue after in situ burning).
    - In all likelihood, bulk sinking is not affected by dispersants. Dispersants would not likely be used on these types of oil.

C. Marine Snow [microbial- and phytoplankton-derived]

Knowns:

1. There are two types of marine snow:
    - Microbial-derived marine oil snow (MDOS): Produced by microorganisms as a by-product of oil biodegradation (Ziervogel et al., 2012; Passow et al., 2012).
    - Phytoplankton-derived marine oil snow (PDOS): Phytoplankton exposed to oil increase production of Transparent Exopolymer Particles (TEP) as a protective mechanism. This TEP emulsifies oil and produces PDOS (Passow, 2014).
2. The planktonic (microbial and phytoplankton) communities exposed to oil produce more TEP, which facilitates the formation of marine snow, which sinks as a result of flocculation processes and can scavenge other suspended materials in the water column (Passow, 2014).
    - Passow (2014) did find inhibition in aggregate formation in the presence of Corexit 9500, which was attributed to inhibition of the organisms that produce TEP.
        - Experiment used WAF created from fresh oil.
        - Santa Barbara water was used for the experiment.
    - Baelum (2012) found no inhibition in aggregate formation for oil alone, oil + Corexit, oil + iron, or oil + iron + Corexit (40 day period). Water collected at 1100 meters during response phase in DWH plume and nearby where there were not any plumes. Fresh Macondo (fresh oil being mixed) and the same Corexit (9500A) were used.

Uncertainties:

1. There is an uncertainty about whether microbial-derived marine snow formation is inhibited by dispersants. It could be a methodological issue (s), such as: type of oil (Macondo oil directly from the well versus collected at the surface (Louisiana sweet crude)), type of water in mesocosms (from 1,100 meters at deepwater plume), and/or time collected (within 48 hours of experiment versus Santa Barbara water of uncertain freshness (bottle effect)).

III. Biodegradation of Oil

Knowns:

1. Hydrocarbon-degrading microbes are ubiquitous.
    - In different geographical locations, differences in microbial community structure exist.
    - Hydrocarbon degraders will actively degrade constituents in crude oil at -1°C in Arctic near-shore surface waters. (McFarlin et al., 2014a)
    - In the GOM and sub-Antarctic (surface water), there is a reported decrease in diversity of microbes and an increase in amount of biomass in deep-water environments (In Water:

Hazen et al., 2010; Mason et al., 2012; Dubinsky et al., 2013) (In Sediment: Mason et al., 2014b).

- Bacterial taxa known to include oil degraders are present in Arctic near shore and off shore environments (McFarlin et al., 2014b).
- A transition in community composition occurs from oil degraders to degraders that can use oil degraders as a food source (Dubinsky et al., 2013).

2. Microbes can either biodegrade oil compounds that are dissolved in water or are present at the water/oil interface.

Uncertainties:

1. The diversity and biomass of microbes in Arctic deepwater environments is uncertain.

IV. Biodegradation of Oil: Pathways

Knowns:

1. Whole oil has an apparent half-life (half-life does not imply first order kinetics).
2. Distinct chemical compounds within the oil have different degradation rates.
   - Asphaltenes and resins are essentially recalcitrant (Prince et al., 2003; Atlas and Bartha, 1997).
   - Some classes of compounds degrade more rapidly than others, depending on environmental conditions (Atlas and Bartha, 1997; Foght et al., 1998).
   - Classification of different compounds in the oil and how they are degraded has been reported; some degrade very slowly, resulting in heavy oil (Aeppli et al., 2014; Head et al., 2014).
   - Arctic biodegradation of crude oil follows a typical biodegradation pattern (McFarlin et al., 2014a).
   - Earlier studies showed similar patterns for cold water (Campo et al., 2013)
3. The different oils (e.g., live vs. dead, light vs. heavy) and suites of compounds within oil are degraded by complex microbial consortia with complementary metabolic pathways.
4. Biodegradation of oil is complex and typically proceeds via a number of steps. It may accumulate as organic metabolites, be assimilated as biomass, or be mineralized to CO_2.
5. There is generally a consistent order for biodegradation of whole oil.
   - The typical biodegradation order is: Alkanes – monoaromatics – PAHs – (parent PAHs) – Alkylated PAHs (Prince, 2003).
   - Lower molecular weight hydrocarbons degrade faster than higher molecular weight hydrocarbons.

- Lindstrom and Braddock (2002) conducted a mineralization experiment with whole and weathered ANS (1400, 4500 ppm) in the presence and absence of Corexit 9500 (1:10, 1:20). Mineralization was measured as CO_2 evolution with radiorespirometry. The experiment was conducted at 8°C in artificial seawater with an enrichment culture obtained from a bunker C fuel spill in beach sand near Dutch Harbor. They reported that Corexit 9500 inhibited the mineralization of hexadecane and phenanthrene. There was no difference among weathered oil or dispersed weathered oil (1:10 or 1:20) treatments.
- McFarlin et al., (2014a) showed the sequence was not altered in the presence of Corexit 9500 and whole oil (GC/MS, -1° C, fresh Arctic seawater, and indigenous community).
- Prince and Butler (2014) showed the sequence was not altered in the presence of Corexit 9500 and whole and weathered oil, (GCMS, fresh New Jersey seawater, indigenous community, 21°C).
- Mason et al., (2014a) showed the sequence was not altered in sediment cores from DWH (radiolabeled constituents from Corexit 9500 and whole oil, 5°C).

Uncertainties:

1. It is uncertain if the biodegradation sequence of oil is relatively consistent in anaerobic seawater environment.
2. The biodegradation sequence of the oil is a function of what constituents are present. Oil type, temperature, and pressure can all affect the fractionation of the oil and therefore the constituents that are present, which may subsequently affect the biodegradation of oil during a spill. (King et al., 2015)
    - Some studies use the whole oil, where there is relatively the same sequence, but this may not be an accurate representation of what is going on in the deep ocean.
    - Changes in the composition of the oil will affect the biodegradation sequence. There may not be any PAHs to degrade in small oil droplets because they weather faster. Large oil droplets that surface would be much higher in PAHs, with limited surface area to volume ratio. Studies show composition of oil in a deep-water plume is dominated by alkanes because of the jetting and dispersant application (King et al., 2015; Hazen et al., 2010; Atlas and Hazen, 2011).
    - Gases going into solution and not in oil droplets may form a bubble. Methane hydrates form a shell around the bubble. It is uncertain if the shell makes the methane hydrates unavailable for biodegradation. At depths less than 500 – 700 meters, the shell melts and gas can go into solution (Spaulding et al., 2000; Giraldo, et al., 2013; Socolofsky et al., 2015).

- There is uncertainty about the sequence of biodegradation and how it is altered by presence of dispersants (this is uncertain regardless of environment, not unique to Arctic).

V. <u>Factors Affecting Biodegradation</u>

Knowns

1. Nutrient and trace metal availability can play important roles in regulating oil biodegradation rates (Pepper et al., 2015).
2. Given existing nutrient levels (e.g. N, P, Fe, Cu, Co); measurable biodegradation of oil in seawater will occur (Delille et al., 2009; McFarlin et al., 2014a).
    - However, oil degradation can become nutrient limited; laboratory studies show that addition of nutrients can accelerate oil degradation (Baelum et al., 2012; Pelletier et al., 2004)
    - Dissolved nitrogen levels vary temporally and spatially in the Arctic from 6-8 µM in the Southern Chukchi Sea to <4 µM within the Beaufort Gyre (Letscher et al., 2012).
    - Anaerobic biodegradation is slower and is less likely to result in complete mineralization than aerobic degradation (Atlas and Bartha, 1997).
    - Under high dilution conditions (low oil concentration), biodegradation should occur given sufficient micronutrient levels.
3. Temperature and microbial community composition impact the rate of biodegradation.
    - While biodegradation of specific oil constituents occurs at lower temperatures (Siron et al., 1995, -1.6 ± 0.2°C; Feller and Gerday, 2003, 4°C; Georlette et al., 2004, 0°C; D'Amico et al. 2006, 2°C; Venosa and Holder, 2007, 5°C; Hazen et al., 2010, 4.7°C; Baelum et al., 2012, 5°C; McFarlin et al., 2014a, -1°C), in general, lower temperatures are associated with lower rates of oil biodegradation.
    - Cold-water-adapted microbes in deep water exhibit higher degradation rates of oil at low temperatures than at high temperatures (Hazen et al., 2010).
    - Psychrophiles can have unique enzymes that exhibit faster kinetics than mesophiles at low temperatures (Moyer and Morita, 2007).
    - In Arctic surface waters, there is a lower range of temperature fluctuation compared to temperate waters. Temperatures in most Arctic marine waters fluctuate between -1.5°C to -1.8°C. Summer inflows from the North Atlantic Current and the Pacific Ocean can raise the temperature in the Norwegian, Barents, and Chukchi seas to as high as 8°C to 12°C (The Arctic, 2015).
4. Microbial bioavailability and differential solubility and physical properties affect biodegradation rates.**

    ** See Physical Transport and Chemical Behavior statements on dissolution.

5. Effect of salinity:
    - In Arctic open water, salinity varies with depth and the pronounced pycnocline (See Physical Transport and Chemical Behavior Statements on salinity)
    - Surface water salinity in the Arctic Ocean and the adjacent shelf seas is relatively low compared to other oceans. In the Arctic Ocean itself, surface salinity varies between 30 and 33 PSU, and can decrease to 26 PSU due to sea-ice melt and river water (Letscher et al. 2012).
    - At the average salinity of seawater (35 PSU) or below, the vast majority of hydrocarbons are biodegradable under aerobic conditions (Prince et al., 2003). However, halophilic oil-degrading organisms have also been described (McGenity, 2010).

Uncertainties:

1. The relative importance of psychrophiles and psychrotrophs to oil biodegradation in the Arctic is unknown.
    - Studies (NRC, 2005) have implied that oil biodegradation rates increase with decreasing droplet size (bioavailability and an increase in surface area to volume ratio at the oil/water interface for microbial colonization).
    - Methods are being developed to create and maintain consistent droplet sizes so that these experiments may be conducted (Brakstad et al., 2015; Kleindienst et al., 2015a).
2. It is uncertain whether all the factors affecting bioavailability and biodegradation impacts are known with respect to:
    - Temperature,
    - Droplet size – surface area/volume ratio,
    - Crude oil composition,
    - Degree of weathering,
    - Present of surfactants (chemical or bio), and
    - Ionic strength.
3. While biodegradation has been documented in a wide range of aqueous environments, we do not know the relationship that changing salinity (near-shore vs. off-shore, river impacts and ice melting) has on biodegradation. There is uncertainty about the relationship between and Arctic oil biodegradation vs. what appears in the literature.
    - Reductions in salinity are more likely to be an impact than increases except in the case of brine channels.
4. There are areas of uncertainty surrounding the effect of certain factors on oil biodegradation in the Arctic (e.g., trace metals in the Arctic, implications of heavier oil sinking in relatively shallow water, oxygen concentration in the presence of ice and oil).

5. The relative importance of microbial community composition vs. the effect of environmental factors on the rate of biodegradation is unknown.
6. Pre-oxidation from sunlight exposure primes hydrocarbon degradation. It is known from other studies with other bio-recalcitrant compounds that pre-oxidation or photolysis will enhance current biodegradation rates (e.g., pharmaceuticals, humic materials) (Keen et al., 2012). The impact of these effects on oil biodegradation in the Arctic is unknown.
7. The effect of temperature is somewhat unknown. McFarlin et al., (2014a) and Prince et al. (2013) measured the percent loss of whole ANS crude oil at different temperatures, but otherwise using the same methods. McFarlin et al., (2014a) used Arctic seawater and conducted the experiment at -1˚C, while Prince et al., (2013) used New Jersey seawater and conducted the experiment at 8˚C. At 24 days, the % loss of oil at 8˚C was 69%. At 28 days, the percent loss of oil at -1˚C was 45%.
8. Biodegradation in ice is assumed to be very slow, but the rates are uncertain.
9. The effect of the formation of OMA on the rate of biodegradation in the Arctic is unknown.
10. Under varying oil concentrations, Corexit 9500 has been shown to increase the initial percent loss of oil due to biodegradation. Below are several studies that showed varying results. (Temperature, oil concentration, type of oil, way it was measured, dispersant type and concentration (DOR), nutrients and oxygen and source of oil).
    - Prince et al., (2013): 8˚C, 2.5 ppm, half-life, percent loss;
    - Prince and Butler (2014): 21˚C;
    - McFarlin et al., (2014a): -1˚C, total oil (dissolved and particulate), 15 ppm, 10 and 28 days;
    - Baelum et al., (2012): 5˚C, 60% degradation with Corexit and 25% without, total oil (dissolved and particulate), 100 ppm 20 days; Lindstrom and Braddock (2002) 1400 – 4500 ppm; Swannell and Daniel (1999) 260 ppm; Davies et al., (2001) 250 ppm; Yoshida et al., (2006) 227 ppm; Zahed et al., (2010) 100-200 ppm; and Venosa and Holder (2007) 830 and 83 ppm.

VI. Effect of Chemical Dispersants on Oil Biodegradation

Knowns:

1. Dispersants will cause the formation of smaller oil droplets than those formed by physical dispersion alone, given the same mixing energy.
    - Field studies show that dispersants form smaller oil droplets (see Efficacy and Effectiveness and Physical Transport and Chemical Behavior documents)
2. Brakstad et al., (2015) showed in a lab study that 10 µm droplets degraded faster than 30 µm droplets.

3. By increasing oil-water-interfacial area, biodegradation of oil can be enhanced by dispersant application compared to biodegradation of oil remaining as a slick on the surface (Prince and Butler, 2014; Prince, 2015).
4. The panel considered a group of papers to be scientifically sound and representative of environmental conditions when it was determining the impact of chemical dispersants on the rate of oil biodegradation (Appendix A). The panel could not agree on the scientific soundness and environmental representativeness of some papers (Appendix B). A subset of the papers in Appendices A and B support the conclusion that some chemical dispersants in current use, such as Corexit 9500, increase oil biodegradation rates. Chemical dispersion was most frequently, but not always, observed to increase oil biodegradation rates over those observed for physically dispersed oil. However, there are a number of caveats to these conclusions:
    - There is a documented publication bias in the sciences against null results (Fanelli, 2010; Franco et al., 2014; Mervis, 2014).
    - Many papers use a proxy to estimate oil degradation (e.g., bacterial production or cell counts vs. direct determination of oil biodegradation) (Kleindeinst et al., 2015b).
    - Changes in the inventory/mass balance of various oil compounds are indicative of biodegradation, but are not unequivocal without appropriate controls and multiple lines of evidence (Garrett et al., 2003).
    - Some studies compare the biodegradation of chemically-dispersed oil to that of physically-dispersed oil, and report that dispersants either enhance (e.g., McFarlin et al., 2014) or slow (Kleindeinst et al., 2015a) oil biodegradation. When reporting differences in biodegradation rates in such comparisons, it is critical to be clear that this is distinctly different from comparing biodegradation of chemically-dispersed oil to that of an oil slick. It is rare in the natural environment, for oil to become physically-dispersed to the extent used in these controlled experiments, therefore this comparison should not be used as a proxy for predicting the outcome of chemically-dispersing a surface slick vs. not dispersing the slick (McFarlin et al., 2014, Prince and Butler, 2014; Prince, 2015).
    - Microcosm or mesocosm studies have inherent value, however, they are unlikely to exactly mimic in situ conditions.

Uncertainties:

1. It is commonly assumed that smaller oil droplets will degrade faster than undispersed oil or larger droplets because of the greater surface area to volume ratio. This is assumed to apply for droplet diameters larger than some threshold diameter (bigger than a microbe). This has not been demonstrated for a range of droplet sizes and oil types. This has only been demonstrated by Brakstad et al., (2015) for 10 vs. 30-micron droplets of Macondo oil with Corexit 9500 and Prince and Butler (2014) (undispersed Alaska North Slope crude

[simulating an oil slick] vs. Alaska North Slope crude dispersed with Corexit 9500); droplet size was not characterized.

2. The impact of chemical dispersants/dispersion on microbial activities (i.e., oil biodegradation) is not well characterized (Kleindeinst et al., 2015a,b).
3. The impacts of chemical dispersants/dispersion on biodegradation in a short-term (episodic release) could be different than a long-term event (e.g., 86 days DWH) where the communities could adapt over time to degrading oil.
4. The concentrations of oil in published laboratory studies are often much greater than those expected in spill situations and this adds to the uncertainties.
    - Recent papers (e.g., Lee et al., 2013; Prince and Butler, 2014) provide an explanation why many studies show contradicting results and that often the test set-up does not represent realistic field conditions. Lab conditions often differ from what you find in a field experiment scale (scalability issue). Dispersed oil is expected to be diluted well below 100 ppm and maybe even below 1 ppm in the water column during a spill.
5. The order in which microorganisms biodegrade various dispersant components versus petroleum hydrocarbons present in crude oil, including the tendency for preferential biodegradation of certain components to occur, is not yet well characterized.

Points of Disagreement

1. Disagreement remained among the committee after reviewing the literature as to whether or not chemical dispersants on the NCP Product Schedule increase, decrease, or do not affect the biodegradation <u>rate</u> of chemically-dispersed oil in comparison to that of physically-dispersed oil.
2. Disagreement remained as to whether the <u>overall amount</u> of oil biodegradation in the presence of dispersants is the same as that of physically-dispersed oil, given the same conditions.

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This document was developed during the period of: January 7, 2015 – Workshop (Seattle, WA) to Final Draft March 17, 2016.

Disclaimer - This "State-of-Science on Dispersant use in Arctic Waters: Degradation & Fate" document presents a compilation of individual opinions of the participants in this session of the State-of-Science for Dispersant Use in Arctic Waters initiative. To the extent that the Federal Government requested certain information, it did so on a purely individual basis. Similarly, the information herein was presented to the Federal Government by individual participants and represent the participants' individual views and policies. Therefore, the statements, positions, and research opinions contained in this document do not reflect any consensus on the part of any of the participants and may not necessarily reflect the views or policies of any individual federal department or agency, including any component of a department or agency that participated in developing this document. No federal endorsement should be inferred.

APPENDIX A

Papers the panel deemed scientifically sound and environmentally representative.

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APPENDIX B

Papers the panel could not agree were scientifically sound and environmentally representative.

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