State-of-the-Science of Dispersants and Dispersed Oil (DDO) in U.S Arctic Waters

1.0 Introduction

Chemical dispersants were employed on an unprecedented scale during the Deepwater Horizon oil spill in the Gulf of Mexico, and could be a response option should a large spill occur in Arctic waters. The use of dispersants in response to that spill raised concerns regarding the need for chemical dispersants, the fate of the oil and dispersants, and their potential impacts on human health and the environment. Concerns remain that would be more evident in the Arctic, where the remoteness and harsh environmental conditions would make a response to any oil spill very difficult. An outcome of a 2013 Arctic oil spill exercise for senior federal agency leadership identified the need for an evaluation of the state-of-the-science of dispersants and dispersed oil (DDO), and a clear delineation of the associated uncertainties that remain, particularly as they apply to Arctic waters.

The National Oceanic and Atmospheric Administration (NOAA), in partnership with the Coastal Response Research Center (CRRC), and in consultation with the U.S. Environmental Protection Agency (EPA) embarked on a project to seek expert review and evaluation of the state-of-the-science and the uncertainties involving DDO. The project focused on five areas and how they might be affected by Arctic conditions: dispersant effectiveness, distribution and fate, transport and chemical behavior, environmental impacts, and public health and safety.

2.0 Objectives

The objectives of the State-of-the-Science of DDO in U.S. Arctic Waters project were to:

- Identify the primary research/reference documents on DDO,
- Determine what is known about the state-of-the-science regarding DDO,
- Determine what uncertainties, knowledge gaps or inconsistencies remain regarding DDO science, and
- Provide recommendations on outreach/education materials needed for senior leadership to be prepared for communicating science regarding dispersant use in spill response.

3.0 Dispersant and Dispersed Oil Databases of Scientific Literature

CRRC created a database that compiled relevant research from 2008 through December 31, 2015. Research documents not published in peer-reviewed scientific publications were included as part of this project if CRRC determined those references were subject to the appropriate review standards for each organization. The CRRC database was continually updated during the project as new research was identified by the expert scientific panels. The database, which is searchable, is available to the public through CRRC along with the subject area documents developed by each of the scientific panels. This effort also looked at the Louisiana University Marine Consortium (LUMCON) database that captured relevant literature prior to June 2008.
4.0 Project Process

The CRRC coordinated a discussion among scientists with dispersant research expertise, as well as those with Arctic expertise, to determine the state-of-the-science (knowns and uncertainties) regarding DDO, as it applies to Arctic waters. Scientific panels for each subject area were selected for their knowledge and expertise in that field. The Project Steering Committee, including the NOAA and EPA Project Liaisons, assisted CRRC in identifying individuals with dispersants and/or Arctic expertise. In developing each of the documents these panels reviewed relevant literature and, based on their expertise, developed statements of knowns and uncertainties regarding each focal topic.

The Steering Committee identified five general subject areas that were deemed important to understanding the State-of-the-Science of DDO. Separate scientific panels convened to focus on each of the following topics:

- Efficacy and Effectiveness;
- Physical Transport and Chemical Behavior;
- Degradation and Fate;
- Eco-Toxicity and Sublethal Impacts; and
- Public Health and Food Safety.

The process was initiated in January 2015 with a five-day workshop being conducted, one day for each subject area. Once established, each scientific panel continued to have regular conference calls over the next two years to continue the literature review and develop the knowns and uncertainties documents for each subject area. Dispersant use policies, including operational issues are not within the scope of this project and are not addressed in these documents.

5.0 Public Input Process

Each of the five subject area draft documents was released for a thirty-day public input period. Reviewers were asked to document their comments or recommend changes, substantiated by a citation of a peer-reviewed research paper. Each scientific panel considered all relevant public input received on the draft documents, and when deemed appropriate, amended the original wording. The final subject review documents were released along with the database for each topic. (A sample public input form can be found here http://crrc.unh.edu/dispersant_science).

6.0 Scientific Panel

The scientific panels consisted of a broad spectrum of national and international experts. Their names are listed at the end of each document.

The scientific panel for Degradation and Fate met initially via face-to-face for 10 hours in January 2015 and then an additional 20+ hours of WebEx meetings (February 2015 to December 2016) reviewing publications, discussing the science, writing/editing the draft document and reviewing and addressing the public input for accuracy. Numerous additional hours were spent by the panelists in preparation for meetings and their individual reviews of the documents.
Disclaimer - This “State-of-the-Science on Dispersant Use in Arctic Waters: Degradation and Fate” document presents a compilation of individual opinions of the participants in this session of the State-of-the-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.

7.0 Degradation and Fate Document

State-of-the-Science for Dispersant Use in Arctic Waters

Degradation and Fate

The topics discussed in this document refer to liquid oil and its associated hydrocarbons and not to gaseous hydrocarbons.

I. Fate of Dispersants

Knowns:

1. Specific components of dispersants have a longer half-life in the environment than other components.
   - Other non-point sources of anthropomorphic 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. For example, persistence in the water column can be affected by depth and other environmental factors and may differ from persistence in sediments.

3. Anionic surfactants based on sulphosuccinates (e.g., DOSS dioctyl sodium sulfo succinate) 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 commercial dispersant mixture except Campo et al. (2013), which deals with Corexit.
   - Using indirect methods, Hamdan and Fulmer (2011) reported that six cultured hydrocarbon-degrading bacteria were inhibited by Corexit 9500, however, the concentrations of the dispersant used ranged from 10 to 100,000 mg/L and included some concentrations that would be higher than those found in the environment during a spill.
4. When dispersants are trapped within weathered oil, some components (e.g., DOSS) may not be readily bioavailable for biodegradation by microorganisms (White et al., 2014).

5. Anionic branched alkyl sulphisuccinates have also been shown to biodegrade under anaerobic conditions, but at much slower rates than under aerobic conditions. Under anaerobic conditions, the linear sulphisuccinates degrade faster than the branched alkyl sulphisuccinates (García et al., 2009; Lee et al., 2011).
   - These data on biodegradation are just for surfactants, not surfactants in a commercial dispersant mixture.

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) 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 the 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. Direct absorption of sunlight by dispersant constituents is poor.
   - Decay in sunlight via mechanisms of photolysis and photo-induced oxidation can occur over a number of days.

10. Natural or anthropogenic organic matter, producing reactive oxygen species in conjunction with sunlight exposure, plays a role in the fate of dispersant components.
    - Organic by-products can be generated from the oil that was spilled.
    - These processes are limited to the depth of water to which UV in sunlight 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 reactive oxygen species present to degrade constituents in dispersants.
Uncertainties:

1. Since dispersant vary in composition, different formulations may vary in their degradation and fate.
2. 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.
3. Products from the decay of dispersants in sunlight are not well characterized and the impact of temperature on the decay process is not well known.
4. 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

General Statement:

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

A. OMA/ OSA*

*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 formation is influenced by a number of environmental factors: oil, suspended material, water column depth, salinity, and mixing energy.
2. In areas with large amounts of sediment in the water column, 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]

During oil spills, biological processes produce extracellular organic compounds that can increase oil solubility in solution and create macro-particles referred to as “marine oil snow” (Passow, 2014). This material differs from marine snow in the absence of oil because it can contain oil. Marine snow gradually accumulates water column particulates making it heavy and causing it to sink.

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; Kleindienst et al., 2015a).
- 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).

Knowns:

1. 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.
     - 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 from 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 offshore 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.
3. The diversity and biomass of oil-degrading microbes in Arctic environments is not as well studied as low temperature deepwater environments in other basins.

Uncertainties:

1. Much of our understanding of oil biodegradation is based on laboratory studies which have inherent value, but it is important to note that laboratory conditions may not accurately reflect environmental conditions.

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 (Atlas and Bartha, 1997; Prince et al., 2003).
   - 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 (McFarlin et al., 2014a) follows a typical biodegradation pattern in temperate and cold water (Campo et al., 2013; Hazen et al., 2010).

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 be: converted to organic metabolites, assimilated as biomass, and/or mineralized to CO₂.

5. There is generally a consistent order for biodegradation of whole oil.

- In general, lower molecular weight hydrocarbons degrade faster than higher molecular weight hydrocarbons and structure affects degradation rate.
- McFarlin et al., (2014a) showed that the sequence in which hydrocarbons in whole oil were biodegraded in near-shore Arctic seawater was not altered in the presence of Corexit 9500 (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 environments.

V. **Factors Affecting Biodegradation**

**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); 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., 2013).

- 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. Generally, microbes are optimized to specific temperature regimes, so temperature and microbial community composition interact to affect biodegradation rates.

• 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. However, 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). The Beaufort Sea surface temperatures can rise to similar values due to shallowness of the water and summer warming. (Johnson et al., 2012)

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 (Letscher et al., 2013), and can be as low as 10 PSU (Beaufort Sea) (Johnson et al., 2012) due to sea-ice melt and river water.

• At the average salinity of seawater (34.7 PSU) (Railsback et al., 1989) 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.
2. Biodegradation in ice is assumed to be very slow, but the rates are uncertain.
3. The effect of the formation of OMA on the rate of biodegradation in the Arctic is unknown.

VI. Effect of Chemical Dispersants on Oil Biodegradation

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).

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. Chemical dispersion was most frequently, but not always, observed to increase oil biodegradation rates over those observed for physically dispersed oil. 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 rate. However, there are a number of caveats to these conclusions:
   - There is a documented publication bias in the sciences against null/negative 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) (Kleindienst 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 (Kleindienst 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. While Corexit 9500 has been shown to increase the initial percent loss of oil due to biodegradation, studies show differing magnitudes of this effect. These differences may be the result of varying experimental design (e.g., 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;

2. It is commonly assumed based on some studies (Brakstad et al., 2015) that smaller oil droplets will degrade faster than larger droplets because of the greater surface area to volume ratio, but the full range of sizes have not been studied, especially very small droplet sizes (less than 10 µm).

3. The impact of chemical dispersants/dispersion on microbial activities (i.e., oil biodegradation) is not well characterized (Kleindienst et al., 2015a, b).

4. The impacts of chemical dispersants/dispersion on microbial communities and their ability to biodegrade oil 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.

5. Many studies show contradicting results and that may relate to test set-ups that do not represent realistic field conditions (e.g., Lee et al., 2013; Prince and Butler, 2014).
   - The concentrations of oil in published laboratory studies are often much greater than those expected in spill situations and this adds to the uncertainties. For example, during the DWH, Lee et al., (2013) reported that “the highest recorded mean oil concentration measured at 1 km from the source was 10 ppm (R/V Brooks McCall; 30 May 2010),
while >10 km the highest mean oil concentration was 3 ppm, with most concentrations in the ppb range (R/V Gordon Gunter; 2 June 2010).

6. 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.
References Cited


Georlette D., Blaise V., Collins T., D’Amico S., and 6 other authors. 2004. Some Like it Cold: Biocatalysis at Low Temperatures. FEMS Microbiology Reviews. 28: 25–42


This panel consisted of:

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APPENDIX A

Papers the panel deemed scientifically sound and environmentally representative.


APPENDIX B

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

Dagnew M. 2004. Rhamnolipid Assisted Dispersion and Biodegradation of Crude Oil Spilled on Water. Degree of Masters of Applied Science at Concordia University, Montreal, Quebec, Canada.


Gilfallan E., Page D., Hanson S., Foster J., and 6 other authors. XXXX. Tidal Area Dispersant Experiment, Seapot, Maine: An Overview.


