The Future of Dispersant Use in Oil Spill Response Initiative

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Coastal Response Research Center

Research Planning Incorporated

National Oceanic and Atmospheric Administration

Coastal Response Research Center

FOREWORD

The National Oceanic and Atmospheric Administration (NOAA) is the primary scientific adviser to the U.S. Coast Guard (USCG), and a trustee for the Nation's marine natural resources. In support of these responsibilities, NOAA conducted an evaluation of the observations and science conducted during the Deepwater Horizon (DWH) spill to build a foundation for planning and decision making in future spills, identify key information gaps and develop a research plan for closing the gaps. This initiative included academic and agency scientists and stakeholders to collect and evaluate the available scientific evidence concerning both surface and subsurface application of dispersants during the DWH emergency response.

To broaden this initiative it is being organized and coordinated under the Interagency Coordinating Committee for Oil Pollution Research (ICCOPR), established under the Oil Pollution Act of 1990. The Coastal Response Research Center (CRRC), a partnership between the University of New Hampshire and NOAA's Office of Response and Restoration (ORR), and Research Planning, Incorporated (RPI) are partnering with NOAA to coordinate and carry out this project.

Contained in this report are: an overview of the information synthesis; expert white papers on dispersant efficacy and effectiveness, degradation of dispersants and dispersed oil, physical transport and chemical behavior of dispersed oil, biological effects of dispersants and dispersed oil on surface and deep ocean species, dispersants and seafood safety, dispersants and human health, and dispersants and risk communication; an independent chemical analysis on the COREXIT dispersants used during the DWH spill; and the outcomes of the workshop.

If you have any comments about the initiative or this report, please contact us. This effort is part of NOAA ORR's on-going activities to improve oil spill response and restoration in the aftermath of Deepwater Horizon and support preparedness for future spills.

Sincerely,

Doug Helton

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UNH Co-Director	Incident Operations Coordinator
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I. Introduction

The explosion and subsequent blowout of the Deepwater Horizon (DWH) offshore drilling rig on 20 April 2010 led to the largest oil spill in United States history and the second largest in the world, with the release of approximately 200 million gallons of light crude oil into the Gulf of Mexico. In response to this *Spill of National Significance*, oil response strategies, including the use of chemical dispersants, were put in place to reduce the amount surface oil reaching shoreline habitats and to minimize impacts to the local biological communities.

At the time of the spill, eight oil dispersants were listed on the National Contingency Plan (NCP) Product Schedule maintained by the U.S. Environmental Protection Agency (EPA). However, only one dispersant brand (COREXIT; Nalco; Naperville, Il) had sufficient stocks and production capabilities to support a spill of this magnitude. Although the contingency plan for the Gulf of Mexico (EPA Regions 4 and 6) pre-authorized the use of several pre-approved product formulations, COREXIT 9527A and COREXIT 9500A were the dispersants of choice. During the DWH response, surface and subsurface operations applied approximately 1,744,152 gallons of dispersants over 84 days. Dispersants were applied at the surface for 61 days (22 April-19 July 2010), and injected at the source (subsurface) for 68 days (30 April-15 July 2010) (Figure 1). Although COREXIT 9500A and COREXIT 9527A were used in the response, the later comprised only 22% (214,669 gallons) of the total dispersant volume, which was only applied at the surface. Daily application volumes averaged 15,949 gallons per day (min-max: 125-56,220) for surface applications, and 11,342 gallons per day (min-max: 2,100-20,655) for subsurface applications.

At a targeted application rate of 5 gallons per acre (1:20 dispersant to oil ratio (DOR) to achieve effective dispersion), surface applications used 56% (972,880 gallons) of the total dispersant volume over an operating area of ~18,000 square miles. Aircraft applied dispersants at an altitude of 50-75 feet and a speed of 150 knots. Operations were restricted to at least 3 nautical miles offshore, with most operations taking place more than 10 nautical miles offshore[1]. Nearly 70% of the dispersant volume was used at the surface during the first month of the response, with surface application rates diminishing, with a few exceptions, for the duration of the response. On 26 May 2010, the EPA directed a decrease in use of dispersant and the cessation of surface applications (Addendum 3 to the Dispersant Monitoring and Assessment Directive). By the end of surface dispersant operations, 412 sorties had applied dispersants on approximately 305 square miles.

Vessels, to a lesser extent, were also involved in the application of dispersants at the surface. Most of their applications concentrated within a 5 nautical mile radius around the former location of the rig at an application rate of 5-20 gallons per acre and a 1:20 DOR. The primary purpose for the vessel dispersant applications was to reduce the concentrations of volatile organic compounds and exposure to workers on the response, drilling, and containment operations near the release site.

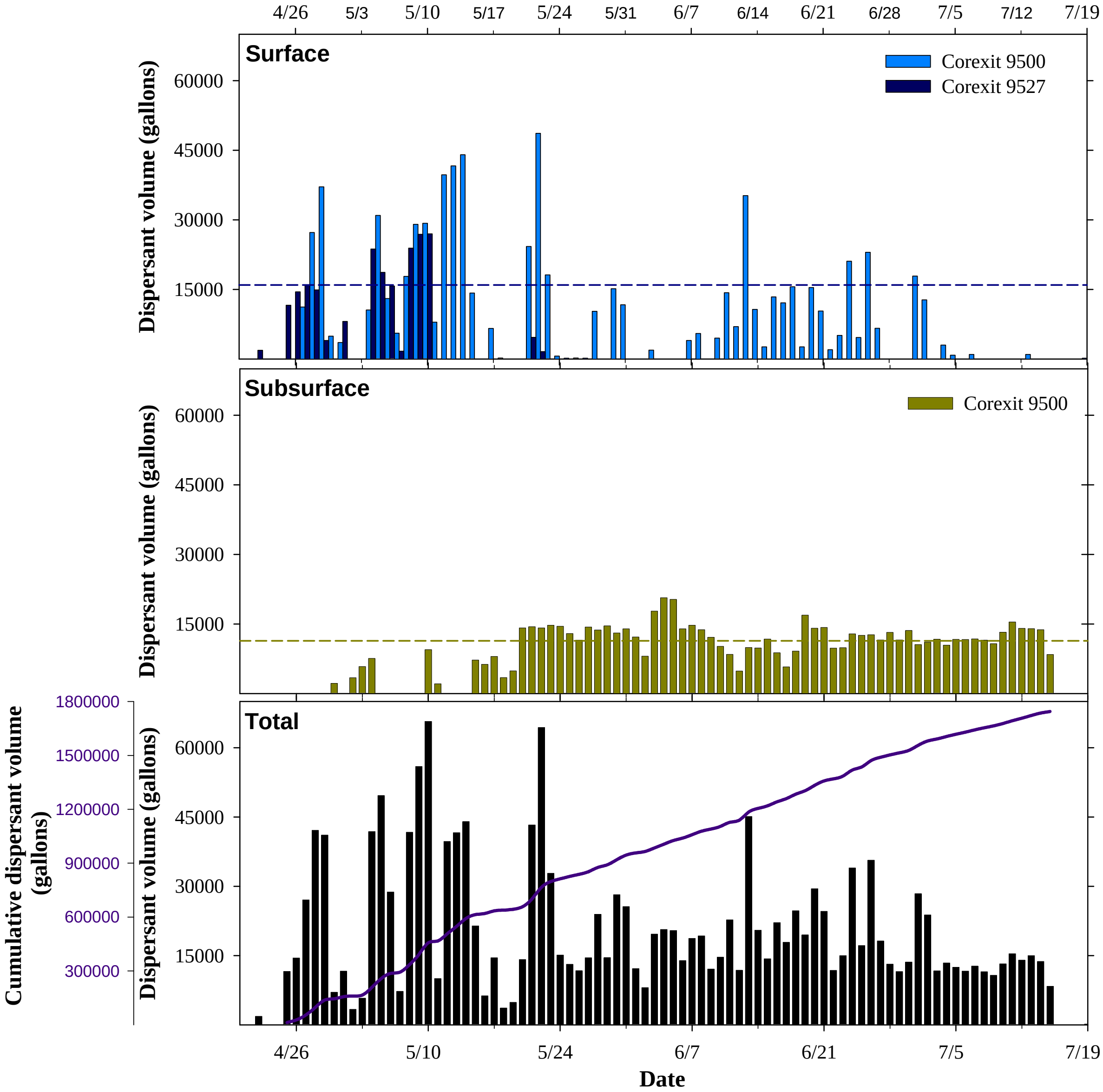

Figure 1. Daily surface and subsurface dispersant application during the Deepwater Horizon oil spill (top and center panels). The dashed lines represent the average surface (blue) and subsurface (dark yellow) applications. The bottom panel represents daily (bars) and cumulative (line) dispersant application totals.

Injection of dispersant at the source (seafloor) was approved by the EPA on 14 May 2010 (Addendum 1 to the Dispersant Monitoring and Assessment Directive) and remained operational for the duration of the release, except for limited periods of time. Starting on 15 May 2010, dispersants were applied at the oil release site through a wand held by a remotely operated vehicle (ROV) at an average dispersant application rate of 8.3 gallons/minute (range: 2.4-14.3 gallons/minute). With a few exceptions, these application rates were below the EPA imposed maximum rate of 15,000 gallons/day (10.4 gallons/minute) (Addendum 3 to the Dispersant Monitoring and Assessment Directive). Based on initial estimates of oil flow rates, the proposed dispersant injection into the plume was 1:20 DOR, but estimates from the available data indicate an average DOR of 1:268 (range: 1:122 to 1:1,200). A total of 771,272 gallons of dispersant were injected into the source during subsea dispersant operations. To date, the precise fate of spilled oil is unknown, including what proportion the escaping oil was chemically or naturally dispersed[2].

Early during the spill the National Oceanic and Atmospheric Administration (NOAA), EPA, other federal agencies, and the academic community were mobilized to locate, monitor, and analyze the behavior and distribution of surface and subsurface oil.[i] These efforts included the monitoring of dispersant application operations and dispersant effectiveness at the surface and at the wellhead. Samples were collected from areas near the wellhead to the coastal zone, and at depths from 5,000 feet (1,500 meters) to the water surface. Water and sediments samples were collected for chemical quantification of total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAH), low molecular weight monoaromatics (benzene, toluene, ethylbenzene, xylene(s); BTEX), dispersant constituents (propylene glycol, di-propylene glycol butyl ether, dioctylsulfosuccinate), fluorometry, dissolved oxygen, temperature and salinity profiles, and small particle analysis (via laser in-situ scattering and transmissometry, LISST) among others. As a result of these large-scale efforts, a significant amount of information was generated increasing the knowledge on deepwater well blowouts.

It is important to note that the light oil from the well underwent natural dispersion even when dispersants were not used. In the Oil Budget Calculator (2010), natural dispersion was estimated to be 13% of the total amount of oil released from the wellhead, with 8% naturally dispersed in the water column from turbulence during the oil’s ascent and 5% dispersed at the sea surface. Natural dispersion on the sea surface was estimated at 5% because the oil that reached the surface was emulsified. Natural dispersion of the unemulsified oil would have been up to 30%.

The unprecedented surface and subsurface use of chemical dispersants during the DHW oil spill raised scientific, public, and political concerns regarding their effectiveness and efficacy, and their potential ecological consequences to aquatic resources. In response to these concerns, NOAA commissioned an initiative to evaluate the large body of information collected during the DWH spill with the goal of building the foundation for planning and decision-making in future spills. A key component of this initiative is to identify key information gaps and develop a research plan to address these gaps.

This initiative was led by the NOAA Office of Response and Restoration (OR&R) and was coordinated with the Interagency Coordinating Committee for Oil Pollution Research (ICCOPR), established under the Oil Pollution Act of 1990. The Coastal Response Research Center (CRRC), a partnership between the University of New Hampshire and OR&R, and Research Planning, Inc. (RPI; Columbia, SC) worked with NOAA to coordinate this project. The project includes the following key elements:

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[i] This effort was part of the operational response. Additional sampling and analysis was conducted pursuant to the Natural Resource Damage Assessment (NRDA).

1. Information Synthesis
    - Compilation of existing information and data on dispersant use collected during the DWH (excluding NRDA data)
    - Expert analysis and review of data and the current state-of-knowledge on the science of dispersants in the form of white papers
    - Review and synthesis of existing dispersant Research and Development (R&D) plans
    - Interagency meetings and discussion
2. Detailed and Independent Chemical Analysis and Characterization of COREXIT Products
    - Analysis of the chemical composition of COREXIT 9500A and 9527A
    - Analysis of the potential risk of chemical constituents to aquatic resources
    - Synthesis of information to address relevant response-related concerns, including COREXIT environmental half-life in the marine environment and its potential bioaccumulation or biomagnification
3. Interagency Representatives, Academic Scientists, Responders, and Stakeholders Focused Workshop
    - Review and discuss information synthesis
    - Identification of data gaps
    - Identification and prioritization of R&D needs
4. Synthesis of Research and Development Needs and Recommendations
    - Compile information obtained in previous project stages
    - Recommendations on moving forward
5. Develop and Implement Dispersant Research Plan
    - Request for proposal development coordinated by CRRC

The following white-paper topics were selected as the framework for the information synthesis and subsequent workshop:

1. Dispersant Efficacy and Effectiveness
2. Degradation of Dispersants and Dispersed Oil
3. Physical Transport/Chemical Behavior of Dispersed Oil
4. Biological Effects of Dispersants on Surface and Deep Ocean Species
5. Dispersants and Seafood Safety
6. Dispersants and Human Heath
7. Dispersants and Risk Communication and Public/Media/Political Perspectives

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[1] After Action Report. Deepwater Horizon MC252 Aerial Dispersant Response. Aerial Dispersant Group December 31, 2010. 80 pp.

[2] Oil Budget Calculator, Deepwater Horizon. Technical Document November 2010. The Federal Interagency Solutions Group, Oil Budget Calculator Science and Engineering Team. 49 pp+app.

II. Overall Project Process

II a. White Papers

Seven teams of federal, academic, and private industry scientists wrote white papers on these topics. The white papers acted as a starting point for discussion during the subsequent workshop. The authors of the papers were given the notes taken during the workshop and revised their papers accordingly. The final white papers are included in this report.

Each team (Table 1) was given a common outline in order to maintain consistency among the white papers, as well as a specific outline for their respective topic. The authors were tasked to address all issues in the outlines and limit their papers to a maximum of ten pages (excluding tables, figures, and references). The common outline consisted of:

- Overview of topic
- Overview of what was known about topic prior to DWH
- Overview in relation to analytical testing/field-monitoring procedures
- Overview of National Research Council and/or CRRC R&D recommendations prior to DWH
- Overview of dispersant use during DWH as it related to the specific topic
- Questions related to topic that were resolved during DWH
- Knowledge gaps and questions that remained un-resolved by DWH
- New questions that resulted from the DWH spill relative to the topic
- R&D needed to resolve outstanding questions relative to topic

Excerpts from each white paper are included in the topic chapters and the unabridged white papers are included in Appendix 1.

Table 1. List of white paper topics and their respective authors.

Topic	Authors
Dispersant Efficacy and Effectiveness	Thomas Coolbaugh, ExxonMobil
	Amy McElroy, U.S. Coast Guard
Degradation of Dispersants and Dispersed Oil	Ken Lee, Fisheries and Oceans Canada
Physical Transport and Chemical Behavior of Dispersed Oil	CJ Beegle-Krause, Research4D
	James Payne, Payne Environmental Services, Inc.
Biological Effects of Dispersants and Dispersed Oil on Surface Water Species and Deep Ocean Species	Adriana Bejarano, Research Planning, Inc.
	Ronald Tjeerdema, University of California Davis, Department of Environmental Toxicology
	Sara Edge, Harbor Branch Oceanographic Inst. at Florida Atlantic University
Dispersants and Seafood Safety	Robert Dickey, Food and Drug Administration
	Walton Dickhoff, NOAA Northwest Fisheries Science Center
Dispersants and Human Health	James Fabisiak, University of Pittsburgh, Department of Environmental and Occupational Health
	Bernard Goldstein, University of Pittsburgh, Department of Environmental and Occupational Health
Dispersants and Risk Communication	Ed Levine, NOAA Office of Response and Restoration
	Steve Picou, University of South Alabama, Department of Sociology, Anthropology and Social Work

II b. Chemical Analysis of COREXIT

Pacific Northwest National Laboratories (PNNL) carried out a detailed and independent chemical analysis and characterization of COREXIT products. This analysis included:

- Analysis of the chemical composition of COREXIT 9500A and 9527A
- Synthesis of information on the environmental fate of COREXIT 9500A AND 9527

II c. Workshop Process

A workshop was convened with the goal of bringing together federal and state representatives, academic scientists, responders, and stakeholders to discuss the future of dispersant use in spill response in the United States. The meeting titled "The Future of Dispersant Use in Spill Response" was held September 20-22, 2011 and hosted by the CRRC and NOAA's Gulf of Mexico Disaster Response Center in Mobile, AL. Present at this workshop were individuals from public, private, local, regional, national, and international institutions with dispersant research or operational expertise. The white papers were discussed by the participants and helped to identify and prioritize dispersant research needs.

The overall goals for the workshop were to:

- Build a fact-based consensus on the trade-offs associated with dispersant use
- Evaluate the current state-of-knowledge on the monitoring, behavior, effects, and fate of dispersants
- Identify information gaps
- Recommend R&D topics to help inform dispersant use in future spill response

As a means to achieve these goals, the workshop consisted of plenary and breakout sessions. During the breakout sessions, each white paper topic was reviewed by a group of experts with a range of perspectives. These groups were presented with guiding questions regarding their respective white paper (e.g., Were there any omissions in the white paper?) and tasked to identify and prioritize R&D needs for their respective topic.

The ultimate outcome of the workshop was a prioritized list of R&D needs. Each of the seven topic groups developed three prioritized R&D needs. These were presented to the entire group in a plenary session and emailed to every participant for review. The culminating day of the workshop, seven new groups were assigned, mixing affiliations, expertise, and perspectives divided from the original topic groups. By using this approach, consensus was reached as objectively and thoroughly as possible with each new group discussing all R&D needs generated the previous day and identifying seven needs as top priority, seven as middle priority, and seven as low priority. The R&D needs developed by each breakout group are included in the topic chapter in this report.

II d. Report and Recommendations

This report compares the R&D needs recommended by previous efforts to those developed during this initiative. Each topic chapter includes the R&D needs identified from the 2005 National Research Council report, the September 2010/November 2011 JITF Oil Spill Response reports, and previous CRRC workshops, a discussion on the unanswered questions that became apparent during the DWH spill, and the R&D needs developed during the September 2011 workshop to address the priority information/data gaps. The conclusion of this report provides a synthesis of the outcome from this initiative, a list of the five R&D needs agreed by the majority of the workshop participants as highest priority, a list of dispersant R&D needs identified by previous efforts (NRC Report and CRRC efforts) and a discussion of next steps. Ultimately, NOAA and CRRC will develop a request for proposal (RFP) based on the outcomes of this initiative and through coordination with ICCOPR to fund research that addresses the key gaps in dispersant information.

Each topic chapter includes: excerpts from the respective white paper (see Appendix 1 for unabridged white papers), an overview of the discussion on what decision makers need to know, any information gaps in these needs, R&D recommendations to fill the gaps, and a list of prioritized R&D needs with accompanying information (i.e., R&D objectives, length of time of project, cost estimation). The notes taken from each breakout group contain a more complete record of the discussion and are included in Appendix 4.

III. Chemical Analysis and Environmental Fate of COREXIT Products

The results of the organic constituent analysis confirms that the major ingredients in the COREXITs are as stated by NALCO on its product web site (http://www.nalco.com/news-and-events/4297.htm). In addition, propylene glycol is identified in Material Safety Data Sheets for COREXIT 9500 and 9527 (http://blog.msdsonline.com) and was detected in the organic analysis. The trace metal concentrations ranged from < 0.005 to 90.5 ug/L. Cu, Ti, and Zn, and to a lesser extent Cr, had particularly elevated concentrations in both dispersants.

For most organic components of the COREXIT products, the available information on environmental persistence and bioaccumulation is sparse, which necessitates some caution in making generalizations about the potential to serve as useful markers or indicators of exposure. It is also worth noting that the COREXIT products are a complex mixture so it is reasonable to expect different degrees of environmental persistence for specific components. Nonetheless, it does appear that all of the major components have relatively short half-lives in the marine environment at surface or shallow depths, on the order of a few days to 10-14 days. The biological and physical mechanisms for loss from the water appear to be varied, due in part to biodegradation and adsorption processes to particulates and sediment. None of the COREXIT organic components have been shown to bioconcentrate to any significant extent. This appears to be also true even for some of the moderately lipophilic components such as DOSS. Although with the latter chemical, research focus has primarily been on edible tissue levels, which is not the most sensitive for monitoring and detection purposes.

IV. Topic Chapters

The following chapters included excerpts from the respective white papers, a summary of discussion during the workshop, and the three prioritized R&D needs developed by the group. The entire white papers are included in Appendix 1 and the notes taken during the breakout session discussion are included in Appendix 4.

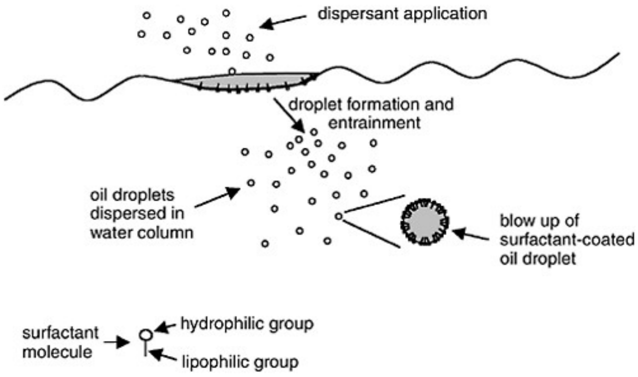
IV a. Dispersant Efficacy and Effectiveness

Workshop Participants
Group Lead: Thomas Coolbaugh, ExxonMobil Research & Engineering
Brad Benggio, NOAA Office of Response and Restoration
Gina Coelho, Ecosystem Management & Associates, Inc.
Ben Fieldhouse, Environment Canada
Charlie Huber, C.A. Huber, Inc.
Vijay John, Tulane University
Rebecca Maker, U.S. Government Accountability Office
Amy McElroy, U.S. Coast Guard
Hung Nguyen, Bureau of Ocean Energy Management
Danny Reible, University of Texas
Jeff Ward, Pacific Northwest National Laboratory

The following section includes excerpts from the dispersant efficacy and effectiveness white paper. The entire white paper can be found in Appendix 1a, including its references.

> *Modern dispersant formulations facilitate natural processes that remove oil from the environment through biodegradation. They are mainly composed of surfactants that reduce interfacial tension between oil and water to allow the formation of micron-sized droplets of oil that are entrained into the water column by wave energy (Figure 3). For comparison, without dispersants, thick oil slicks generate millimeter-sized droplets when impacted by waves. These larger droplets tend to rapidly rise back to the surface where they coalesce and reform the slick. The smaller droplets (e.g., 70 microns) formed after applying dispersants remain in the water column and become a concentrated energy source for oil-degrading bacteria. Marine environments around the world contain oil degrading bacteria that have evolved to consume oil released by natural seeps.*

Figure 3 – Mechanism of Chemical Dispersion (National Research Council)[4]



> *A misperception about dispersants is that they cause oil droplets to rapidly sink to the seabed. This is not the case since dispersants are less dense than sea water and dispersed oil droplets remain positively buoyant unless they encounter and associate with heavier marine sediments or lose significant amounts of their lighter components via dissolution, evaporation or degradation. In marine waters far from shore, encountering enough sediment to rapidly sink large quantities of dispersed oil is unlikely. The droplets generated after applying dispersants range in size from a few microns up to 100 microns in diameter. The rise velocities of these droplets are insignificant compared to the turbulence found in the open ocean. If these droplets become negatively buoyant through degradation or dissolution, they would be even smaller with very low fall velocities. The end result is that once dispersed oil enters the water column, it tends to remain entrained without resurfacing or falling to the seabed until it is removed from the environment through biodegradation.*
>
> *Effectiveness tests are performed to determine if a dispersant can disperse a specific type of oil. These tests are conducted in closed systems, e.g., lab beakers or large wave basins, and for short durations, i.e., from a couple of minutes for some lab tests to 30 minutes for some wave-basin tests. Although it takes time, oil can spread to an extremely thin layer at sea, whereas beakers and basins keep oil artificially thick by limiting its natural tendency to spread. Constraining both time and surface area in dispersant efficacy tests can lead to underestimation of effectiveness because a) more viscous oils such as weathered crudes or water-in-oil emulsions take more than a few minutes to disperse and, b) thin oils disperse more easily than thick oils. In low-energy conditions, the dispersion process can take longer as well because oils must spread thinner before they disperse.*
>
> *Currently six basic laboratory efficacy tests are routinely employed to evaluate the performance of dispersants. Each test method has its own distinct characteristics and care should be taken to when comparing results between them. While the numerical results of these tests are useful for comparing dispersants on a relative basis, they may not be representative of actual performance expected at sea; clearly there is room for harmonizing testing methodologies.*
>
> *The large scale use of dispersants during the Deepwater Horizon incident has helped identify the need for a thorough review of the understanding of this response option. This is especially true with respect to its efficacy in minimizing environmental impacts, identification of the products that may be most effective, the environmental conditions under which dispersants are most effective, and the factors that most influence their performance. Information that results from such a technical review will allow for the identification and description of key areas that will be most amenable to new or continuing research.*

The dispersant efficacy and effectiveness group identified subsurface dispersant use as a technology area with the largest information gap. Decision makers need to know how effective a dispersant will be when applied to various types of oil and at various conditions (e.g., depth, temperature, pressure). Currently, there is a basic understanding of how dispersants interact with oil when applied beneath the surface because of the large amount of data from surface use of dispersants, but there is a need to know more about the specifics of subsea use. The group recommends research in this area, specifically on improving the capacity to monitor in real-time the interactions of oil and dispersants in the subsurface, a quantitative method to measure effectiveness in the subsurface, and study the overall characteristics of dispersants in the subsurface at various temperatures and pressures, and with specific oil types and flow regimes, e.g., flow rate, droplet size, turbulence and proximity of dispersant introduction. Other decision maker needs include, ongoing updated information during a response in real time, information that is available in a usable format, and valid monitoring results of dispersants for use in the decision-making process (e.g., use of the SMART protocol or some analogous methodology). Remote monitoring technologies and a widely accepted, consistent information management system are important tools for decision makers. With the advent of the possibility of subsea dispersant use, protocols for information management and the decision-making process in general, should be adapted to include its use during an oil spill response. Tables 2, 3, and 4 show the three priority R&D needs identified by the group.

Table 2. Dispersant Efficacy and Effectiveness R&D Need Priority 1.

Research Topic	**Subsea Dispersant Effectiveness**
Objectives	- Define the conditions of operability for dispersant use: • Characteristics of dispersant to apply • Physical parameters of when to apply, considering flow rate, dispersion mechanism, dispersant to oil ration (DOR) • Study effectiveness for various types of oil and specific characteristics of the release at the source - Confirm volatile organic compound (VOC) reduction at the surface as a key aspect of worker safety • Potential Health and Safety (H&S) project • Potential effect on spill response operations, e.g., continued relief well operations
Guidelines	- Coordination with other ongoing R&D efforts (e.g., API JITF) - Lab-scale testing→meso-scale tests→field trials
Issues/Problems	- Wide range of potential release conditions to be considered (e.g., volume, pressure, depth, oil characteristics, gas to oil ratio) - Specialized facilities required for deep sea conditions (e.g., need for high pressure to be evaluated, scalability of test results) - Permits for field trials
Application to Decision Making Process	- Efficiency of response - Identification of trade-offs - Reduction of uncertainty - Identifying technology requirements and equipment needs - Worker safety benefits from reduced VOC exposure, ability to continue surface response activities
Length of Time of Project	>2 years
Total Cost Estimate	High, > $400,000

Table 3. Dispersant Efficacy and Effectiveness R&D Need Priority 2.

Research Topic	Innovative Analytical Techniques For Surface and Subsurface
Objectives	- Improve aerial surveillance for identifying thick oil (surface) - Improve targeting of thick oil (surface) - Improve instrumentation for measuring dispersant effectiveness both on the surface and subsea (e.g., ROV's) - Availability of information during response in real-time - Refine SMART protocol and operational need/value duringsubsea and surface response based on recent experiences
Guidelines	- Coordination with other ongoing R&D efforts (e.g., API JITF, OGP) - Labtests→meso-scale testing→field trials
Issues/Problems	- Testing a wide range of technologies, some more advanced/accepted than others - Inherent operational and technological limitations of specific technologies - Scalability and suitability from lab to field - Permits for field studies
Application to Decision Making Process	- Significant potential for improved operational effectiveness - Supports decision making process of continued use - Tool to document extent of release and response success
Length of Time of Project	>2 years
Total Cost Estimate	High, > $400,000

Table 4. Dispersant Efficacy and Effectiveness R&D Need Priority 3.

Research Topic	New Dispersant Formulations
Objectives	- Develop new highly effective dispersants for use in different extreme environments - Evaluate need for separate subsea specific dispersant
Guidelines	- Consider range of environmental parameters, e.g., depth, pressure, temperature, presence of ice - Consider the use of environmentally benign materials - Design for use in existing hardware
Issues/Problems	- Product testing/registration/approval - Availability of large scale production - Scalability from lab to field - Permits for field studies
Application to Decision Making Process	Address stakeholder concerns about existing approved products Possibility of enhanced product performance
Length of Time of Project	>2 years
Total Cost Estimate	High, > $400,000

IV b. Degradation of Dispersants and Dispersed Oil

Workshop Participants:
Group Lead: Robert Pond, U.S. Coast Guard
Victoria Broje, Shell
Cort Cooper, Chevron Energy Technology Co.
Elizabeth Erdmann, U.S. Government Accountability Office
Terry Hazen, Lawrence Berkeley Laboratory
Ken Lee, Fisheries and Oceans Canada
Jacqueline Michel, Research Planning Inc.
Irv Schultz, Pacific Northwest National Laboratory
James Staves, U.S. Environmental Protection Agency

The following section includes excerpts from the dispersant degradation white paper. The entire white paper can be found in Appendix 1b, including its references.

> *Any discussion on the biodegradation of chemically-dispersed oil must consider the degradation of the oil itself. A variety of microorganisms in both terrestrial and marine environments have the capacity to utilize petroleum hydrocarbons as the sole source of carbon and energy (Head et al., 2006; Leahy and Colwell, 1990; Atlas, 1981, 1984; ZoBell, 1973). Recently 181 genera of bacteria, 163 genera of filamentous fungi and yeast, and 22 genera of algae have been identified to have the ability to degrade hydrocarbons by metabolizing them in order to grow (Prince, 2010a,b). These findings are not surprising considering the fact that marine microorganisms have long been exposed to significant quantities of petroleum hydrocarbons from natural seepages.*
>
> *From 1990 to 1999, approximately 600,000 tons of petroleum were released into the world's oceans per year from natural seepages (NRC, 2003; Stout and Wang, 2008). Biodegradation by indigenous microbial communities is the major process responsible for the weathering and eventual removal of oil from natural seeps that enters the marine environment (Atlas, 1995; Atlas and Bartha, 1992; Leahy and Colwell, 1990). Within the marine environment, bacteria are the predominant hydrocarbon degraders (Head et al., 2006; Venosa and Zhu, 2003). Studies from tropical to cold Antarctic and Arctic environments have verified their ubiquitous distribution and their ability to multiply rapidly upon the introduction of oil (Atlas, 1995).*
>
> *Biodegradation rates have been shown to be the highest for saturates, followed by light aromatics, with high-molecular-weight aromatics and polar compounds exhibiting extremely low biodegradation rates (Prince, 2010c). Co-metabolism plays an important role in oil biodegradation and may require microbial consortia or syntrophic interspecies cooperation (McInerney et al., 2008). Many complex branched, cyclic, and aromatic hydrocarbons, which otherwise would not be biodegraded individually, can be oxidized through co-metabolism in an oil mixture*

due to the abundance of other substrates that can be metabolized easily within the oil (Atlas, 1981).

It is important to note that microorganisms produce extracellular biosurfactants to promote the formation of oil-in-water emulsions that aid in the uptake and subsequent degradation of hydrocarbons (Desai and Banat, 1997). The hydrophilic and hydrophobic components within the biosurfactants emulsify hydrophobic hydrocarbons, and allow for transport into the hydrophilic intracellular space for biodegradation (Southam et al., 2001). In addition, the fatty acid moieties of biosurfactants promote the growth of microorganisms on the surface of oil droplets (Rosenberg et al., 1979). Nikolopoulou and Kalogerakis (2008) reported that the use of rhamnolipid biosurfactants increased removal of weathered petroleum hydrocarbons (96% removal of C19–C34 n-alkanes within a period of 18 days) and reduced the lag phase prior to the onset of biodegradation. Saeki et al. (2009) showed that addition of biosurfactant JE1058BS to seawater stimulated the degradation of weathered Alaska North Slope 521 crude oil by stimulating the activity of the indigenous marine bacteria and facilitating the removal of oil from the surface of contaminated marine sediments.

In terms of the influence of environmental factors controlling natural oil biodegradation rates, field studies have shown that active microorganisms living in low-temperature environments are dominated by two groups: psychrophilic and psychrotolerant, which are sometimes called psychrotrophic (Atlas, 1984). As defined by Morita (1975), psychrophiles experience optimum growth at less than 15°C, with a maximum growth temperature below 20°C and a minimum growth temperature at or below 0°C. Despite living at these low temperatures, psychrophiles often have metabolic rates comparable to those displayed by the mesophiles adapted to more moderate temperatures. For example, Delille et al. (2009) reported that a temperature of 4°C in the Antarctic had little effect on biodegradation efficiency and that the nutrients, nitrogen and phosphorus, were the limiting factors. Results obtained by Siron et al. (1995) indicated that the temperature threshold for observing significant oil biodegradation was around 0°C. Decreases in solubility associated with low temperatures were considered to be a causal factor for the cases of observed recalcitrance of hydrophobic compounds in cold-water. However, recent reports have indicated that some bacteria may have adapted to the low solubility of hydrophobic environmental chemicals (Deppe et al., 2005; Wick et al., 2002). Indeed there is now evidence that hydrocarbon-degrading microbes may have novel uptake mechanisms that enable them to degrade hydrocarbons at rates that exceed their rates of dissolution in the aqueous phase (Leahy and Colwell, 1990; Thomas et al., 1986).

Throughout the world, the salinity of seawater averages about 35‰ (parts per thousand). Salinity variations, albeit small, are mainly caused by such factors as melting of ice, inflow of river water, evaporation, rain, snowfall, wind, wave action, and ocean currents that cause horizontal and vertical mixing of the saltwater (Lagerloef et al., 1995). Most marine species have an optimum salinity range of 25–35‰ (ZoBell, 1973) and species living in the transition environments are well

> *adapted to fluctuations in salinity. Microorganisms requiring salt for growth are referred to as halophiles. Whereas halophilic hydrocarbon-metabolizing bacteria perform well in this salinity range, there have been reports of the isolation of bacteria capable of degrading hydrocarbons above a salinity of 35‰. Bertrand et al. (1990) reported the isolation from a salt marsh of an extremely halophilic archaea bacterium capable of degrading hydrocarbons in 204‰ NaCl, but not below 105‰. Diaz (2008) reported the isolation of a bacterial consortium, which mainly included members of the genera Marinobacter, Erwinia and Bacillus, from a crude oil sample from the Cormorant field in the North Sea. This consortium was able to metabolize petroleum hydrocarbons in a salinity range from 0 to 220‰ NaCl. Total oil degradation ranged from 48% to 75%, with the greater degradation occurring at the lower salinities.*
>
> *At the sea surface, wind and wave action maintain a constant supply of oxygen, thus aerobic catabolism of hydrocarbons is usually the preferred biochemical pathway (Leahy and Colwell, 1990). Oxygen may become limiting in subsurface sediments and anoxic zones of the water column. Oxygen limitation is also a concern for most fine-grained marine shorelines, freshwater wetlands, mudflats and salt marshes (Venosa et al., 2002a; Venosa and Zhu, 2003). It is commonly believed that biodegradation rates under anaerobic conditions are almost negligible, while aerobic biodegradation of hydrocarbons occurs rapidly. However, the importance of anaerobic biodegradation should not be underestimated as it has been shown to be a major process under certain conditions. In anoxic marine sediments, reductions of sulphate, Mn(IV) and Fe(III) are the primary terminal electron-accepting processes (Canfield et al., 2005; Finke et al., 2007). Hydrocarbon degradation coupled with sulphate reduction prevails in marine anoxic sediments (Lovley et al., 1997).*
>
> *With recent advances in analytical methods such as genomics, we are now able to determine the potential of whole microbial communities for oil biodegradation at low temperatures. New evidence as a result of advances in the field of environmental genomics suggests that crude oils are degraded by indigenous organisms in cold water environments at a higher rate than previously reported. This is not surprising since natural oil seeps occur in the world's oceans at great depths and low temperatures – microbes have become well adapted to their surrounding environment. Studies have conclusively shown that elevated concentrations of hydrocarbons in the environment increase the number of catabolic-gene copies among the microbial community (Heiss-Blanquet et al., 2005; Stapleton and Sayler, 2000; Whyte et al., 2002).*

The dispersant degradation group discussed various decision maker needs: the understanding of various degradation mechanisms, the long-term fate of a dispersed oil plume and whether it is being degraded, and methods to verify the degradation of dispersants and dispersed oil. The R&D needs which arose during this discussion were: determine the significance of photo-degradation and other weathering processes with the presence of dispersants, improve in the understanding of the interactions between chemically dispersed oil and suspended material, develop tools that provide supporting evidence during an event on the degradation of dispersants and dispersed oil, conduct field experiments investigating changes in microbial community structure and function from dispersants, improve the understanding of biodegradation rates and interactions between various types of oil and dispersants at various environmental conditions.

The group developed only two R&D needs from their discussion; however, their first priority is a very extensive topic and consolidates many of the R&D needs. Tables 5 and 6 show the research topics.

Table 5. Degradation of Dispersants and Dispersed Oil R&D Need Priority 1.

Research Topic	**Degradation Rates of Dispersed Oil**
Objectives	A research program on quantification of degradation rates of chemically dispersed, physically dispersed, and undispersed oil
Guidelines	- Compare oil degradation on surface vs. shoreline vs. water column vs. sediment - Develop analytical protocols for detection of chemical dispersants and degradation rates under variable environmental conditions - Develop the ability to conduct "science of opportunity" from unanticipated spills, R&D response team - Conduct field experiments (changes in microbial community structure and function, fluorescence, stable isotope analysis) to assess the influence of suspended particulate material on dispersed oil degradation - Develop and apply tools including models that provide multiple lines of supporting evidence during actual spill events (e.g., analytical tracers) - Determine the significance of photo-degradation and other weathering processes in the presence of dispersants to support integration of biodegradation rates into predictive models -Study biodegradation of oil in the presence of deep sea dispersant injection
Issues/Problems/ Opportunity	- Expensive, requires a well-coordinated, multi-disciplinary effort. Needs to be coordinated with other R&D efforts on issues like fate and transport, modeling, biological effects, etc. - National funding programs such as the Environmental Security Technology Certification Program (ESTCP) and Strategic Environmental Research and Development Program (SERDP) may be funding sources
Application to Decision Making Process	Provides critical information related to oil degradation required for the development of operational guidelines
Length of Time of Project	>5 years Key milestones and deliverables along the way
Total Cost Estimate	High, > $400,000 - Looking at 9 individual projects each funded in the medium-high range - Expectation that these projects will be leveraged with other funding and national user facilities

Table 6. Degradation of Dispersants and Dispersed Oil R&D Need Priority 2.

Research Topic	**Effect of Sub-sea Dispersant Application on Water-soluble Hydrocarbons**
Objectives	Impact of chemical dispersants on the dissolution/degradation of water soluble hydrocarbons including VOCs from subsea releases
Guidelines	- Re-evaluation of existing DWH data - Lab experiments to fill data gaps - Design a study plan for either spill of opportunity or controlled experimental spill
Issues/Problems	- Spills of opportunity only represent a specific situation - Human health concerns
Application to decision making process	- Supports FOSC decision to apply dispersants to protect human health
Length of Time of Project	1-2 years (potential for 1 year)
Total Cost Estimate	Medium, $100,000 - $400,000

IV c. Physical Transport and Chemical Behavior of Dispersed Oil

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The following section includes excerpts from the physical transport and chemical behavior white paper. The entire white paper can be found in Appendix 1c, including its references.

> *Transport of chemically dispersed oil at the surface is downward, into the mixed layer, where we have a conceptual model that wind and wave induced mixing move the dispersant and any dispersed oil vertically into the water column, and, in general, droplets less than 70-100 μm in diameter do not resurface. Concentration variations are primarily related to surface initial conditions, e.g. oil (x,y, thickness, t), chemical dispersant (x,y, concentration, t), wind (x,y,z-0,t), and waves (x,y,t). In the subsurface, particularly the deep ocean, vertical mixing is very low, so, inert chemicals put into the water column travel along the density surface with little mixing. The Deepwater Horizon MC 252 well, and much of the U.S. deepwater development, is located along the Louisiana-Texas continental slope. The circulation along the continental slope is complex. These dynamics affect bottom water movement and, thus advection of*

> *dissolved constituents and tiny oil droplets (with rise velocities on the order of weeks to months). In the surface mixed layer, droplets less than 100 μm are viewed as too small to rise against the turbulent mixing. In the deep ocean, the turbulence is much less (Ledwell and Hickey, 1995, Ledwell and Bratkovich, 1995, and Ledwell, Watson and Law, 1993).*
>
> *During the Deepwater Horizon oil spill, dispersants were also injected into the oil plume at the release point into the water column, first from the broken riser and then from the cut riser at 1,500 m. During an oil spill response, we do not have near-real-time information on mixing energy, target or actual dispersant-oil-ratios (DOR), the duration of oil-dispersant interactions, dispersant efficiency, oil droplet size distributions, or identification of physically- vs. chemically-dispersed oil available for decision makers. However, analyses and data to date do indicate that much of the transition from the multiphase gas-oil plume to separate oil and gas bubble phases occurred between 1000 - 1300 m (Socolofsky et al. (2011), see also Yapa et al. (2001)). This layer is the subject of continuing reporting from the Joint Analysis Group (JAG, 2010a, b, c), including a summary report to be completed by the end of 2011.*
>
> *The separation of oil droplets and gas bubbles from the multiphase flow from the well was accompanied by almost complete dissolution of lower molecular-weight-aliphatics (through heptane, McAuliffe, 1987) and lower-molecular-weight aromatics (alkylated benzenes) (Reddy et al., 2011), with more limited dissolution of two- and three-ring aromatics (alkylated naphthalenes, phenanthrenes/anthracenes, and dibenzothiophenes). Camilli et al. (2010) tracked this subsurface plume at depth for over 35 km, and literally thousands of water-column samples collected during numerous Response- and NRDA-cruises have provided measurements of BTEX and PAH distributions throughout the water column. Figures 1 and 2 show dispersant indicators (2-butoxyethanol, glycol ethers, and bis-(2-ethylhexyl) fumerate) and selected BTEX and PAH constituents from the public Operational Science Advisory Team (OSAT) and GeoPlatform.gov data sources. Dissolution kinetics rapidly increase as the oil droplet surface-area-to-volume-ratio increases (i.e., as the droplet sizes get smaller). The intention of the subsurface dispersant application was to transition oil mass from larger to smaller droplet sizes. Presumably, if the subsurface injection of dispersants was effective, dissolution kinetics would have been enhanced, but research is needed to develop methods to be able to evaluate effectiveness on a response time-scale.*

The physical transport and chemical behavior group developed a detailed list of R&D needs, some of these include methods for measuring parameters in the surface and subsurface, extending environmental sensitivity index (ESI) maps into the subsurface, conducting an analysis of chemistry data and photographic evidence from DWH, and improving the understanding of dispersed oil droplet behavior. The full list of R&D needs is included in the appendix to this report.

The group narrowed their list of needs down to three key potential projects. They are shown in the Tables 7, 8 and 9.

Table 7. Physical Transport and Chemical Behavior of Dispersed Oil R&D Need Priority 1.

Research Topic	Data Mining for Dispersant Information from DWH
Objectives	- Correlating quantitative information on subsurface dispersant effectiveness and dispersant application time series - Correlating the subsurface injection with emulsification at the surface - Examining the chemistry data for individual dispersant components in the oil droplets during the DWH spill
Guidelines	Use existing data from wide variety of sources: - JAG - OSAT - NRDA - Field Observation: overflights, etc. - Remote sensing: Ocean Imaging, AVIRIS, Satellite
Issues/Problems	Access to NRDA data and completion of laboratory analyses
Application to decision making process	Will help answer the question of whether subsea dispersant application was/is effective, and how effective.
Length of Time of Project	1-2 years
Total Cost Estimate	Medium, $100,000 - $400,000

Table 8. Physical Transport and Chemical Behavior of Dispersed Oil R&D Need Priority 2.

Research Topic	Determine the Role of Dispersants on Transport, Dissolution, Leaching, and Biodegradation Processes
Objectives	- Effect of dispersants on droplet size/bubble size distribution and the trapping height of plume - Interactions of chemically dispersed oil droplets with suspended particulate matter and the effect of these processes on the rate of oil biodegradation and fate - Degree, rate, and consequence of surfactant leaching from chemically dispersed oil droplets - Role of dispersants on the dissolution process (short and long term) - How subsurface application of dispersants affects characteristics of that oil at the surface - Differences in the effects of photolysis on chemically and physically dispersed oil droplets
Guidelines	- Surface and subsurface (turbulence regimes quite different) - Consider pressure and temperature effects on surfactant leaching
Issues/Problems	Many sub-topics Could be dependent on individual oil and dispersant chemistry
Application to decision making process	Dispersant use is all about trade-offs: These processes or not well enough understood to model the ultimate effects of dispersants – better modeling could be used to help decision makers evaluate trade offs
Length of Time of Project	>2 years
Total Cost Estimate	High, > $400,000

Table 9. Physical Transport and Chemical Behavior of Dispersed Oil R&D Need Priority 3.

Research Topic	**Development of Localized Integrative Models and Decision Support Tools for Planning and Response**
Objectives	- Improve existing models - Integrate biological and physical transport models - Make models useable/accessible for decision makers and planners - Used to inform the general public
Guidelines	Geared for decision makers: not researchers Integration is key – decision makers need to evaluate trade-offs of complete process
Issues/Problems	Need local support for data and funding Each project would only support one local region
Application to decision making process	Evaluation of trade-offs requires integrated analysis of impacts: – Impacts are dependent on local conditions – Models cannot be set-up in a response time-scale, but if they exist, can be used both during planning and response
Length of Time of Project	2 years
Total Cost Estimate	High, > $400,000 (but scalable)

IV d. Biological Effects of Dispersants and Dispersed Oil on Surface Water Species and Deep Ocean Species

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The following section includes excerpts from the biological effects white paper. The entire white paper can be found in Appendix 1d, including its references.

> *Dispersant use is usually considered by spill responders when other means of response, such as containment and removal, are not deemed to be adequate[1]. For instance, during the Deepwater Horizon (DWH) spill dispersants were quickly employed when it became apparent that other means of response were insufficient[2]. However, there are usually consequences for both hydrocarbon bioavailability and toxic impacts, thus environmental tradeoffs must be evaluated. For instance, while*

undispersed oil generally poses the greatest threat to shorelines and surface-dwelling organisms, most dispersed oil remains in the water column where it mainly threatens pelagic and benthic organisms[1]. This tradeoff was a prime consideration during the DWH spill[3].

Prior to the DWH, many studies were done on the toxicity of dispersants (primarily Corexit 9527 and 9500) and dispersed oil ([1, 53] and references therein; [54-56]). Although studies have filled critical data gaps in the knowledge and understanding on the effects of dispersants (for example[57, 58]), the experience from the DWH clearly showed that many of the data gaps identified earlier[1, 53] still persist. In this section we build upon the NRC recommendations for additional studies based on the state of knowledge prior to and after the DWH. However, an independent effort should focus on reviewing and evaluating knowledge gaps and gains from past spills (controlled or accidental) involving the use of dispersants.

General Data Gaps

Significant advances in the understanding of dispersant efficacy have been gained since the recommendations of the NRC and subsequent reports. However, all the recommendations regarding fate and effects are still relevant. Specific data gaps include: photo-enhanced toxicity; relative contribution of dissolved and particulate oil phases to toxicity; interaction of dispersed oil with sediment particles and effects to benthic fauna; tests with representative species, sensitive species and different life stages; toxicity tests that addresses delayed effects; exposures through different routes; toxicity from pathways other than narcosis (e.g., oxidative products, receptor-mediated pathways associated dissolved fractions, and smothering by oil droplets); and long-term effects on population and communities.

Comparing oil/dispersant toxicity across studies can be a challenge. Not only the preparation of WAFs and CEWAFs has differed over the years (e.g., differences in mixing energies, settling times, media treatments- filtered vs. unfiltered), but also have exposure conditions (static vs. flow-thru, closed vs. open systems, constant vs. spiked), and chemical analysis of exposure media (nominal vs. measured, particulates vs. dissolved phases, TPAH vs. TPH). Consequently, making comparative use of the existing toxicity data is almost impossible. Efforts should continue to support standardization methods and procedures (e.g., CROSERF or similar) that would allow greater comparability and reproducibility of toxicological data, and a more certain use of experimental data as scientific decision tools in future spills.

Toxicity testing under constant exposures (e.g., LC_{50} tests) does not realistically and adequately assess the risk to aquatic receptors. Under field conditions, organisms are likely exposed to multiple stressors at any given time, which could result in additive, synergistic, or antagonistic effects. But dynamic environments are expected to dilute and mix the water column, resulting in rapidly declining exposure concentrations. However, constant exposures tests may serve as conservative estimates of toxicity. The traditional constant exposure durations in standard LC_{50} (48 or 96 hours) tests *should be compared to the much shorter (a few hours) and rapidly declining exposures experienced by marine organisms when oil is dispersed in open waters.*

Analyses of biological effects following an oil spill have not typically focused on the effects from chronic exposures to extremely low concentrations, or have explored the potential of changes in behavioral responses (e.g., olfactory, time-response to stimuli) as indicators of exposure. These endpoints are relevant as these can lead to measurable effects at the population and community levels (e.g., increased predation; subtle changes in trophic structure and links), and should be considered in future spills.

Although chemical analyses used in spill response typically follow recommended protocols, standardization of such techniques throughout the response should be considered. Standardization of such procedures extends to the separation of dissolved vs. particulate oil phases, the use of chemical signatures, analysis of a whole suite of PAHs (beyond the 16 priority PAHs), as well as analysis of TPHs, and dispersant indicators. Efforts should also discuss acceptable method detection limits.

Data Gaps from the DWH

Temporal and spatial sampling intensity throughout the duration of the spill response should be considered when evaluating and interpreting short- and long-term effects to aquatic receptors. Although several thousand samples were collected for the detection and characterization of oil constituents, sampling efforts specific to dispersants and dispersed oil were limited, and varied substantially over space and time.

The effects of low temperature and high pressures on both physically and chemically dispersed oil and dispersants are not well understood, and therefore their fate and effects in deep waters constitute a significant data gap. Although much information was gained from the DWH on the effect of dispersants on droplet size distribution at depth, future studies should focus on the correlation between oil droplet size distribution and oil constituent bioavailability and toxicity, particularly on the toxicological effects resulting from exposures to dissolved vs. particulate oil. Another question that remains unanswered is the fate and effects of oil at depth if injection of dispersants at the wellhead had not occurred.

Most toxicity testing of dispersant and dispersed oil during the DWH response focused on 2 or 3 species, which have limited capabilities when characterizing risks to several hundred likely receptors. In addition, these tests did not sufficiently address potential differences in sensitivity to organisms living in the water-column in the Gulf of Mexico. Furthermore, the toxicity testing conducted during the response did not address the potential effects of dispersants and dispersed oil to deepwater species inhabiting areas where low temperatures can inhibit or reduce biodegradation and affect uptake and depuration kinetics. Sediment sampling of offshore deepwater bottoms was relatively limited, and so were the toxicity testing of these samples. Thus, these efforts may have not adequately quantified the impacts of subsurface injection

> *of dispersants on these habitats, though assessments can use the state of knowledge from other spills (e.g., IXTOC, Sea Empress, Montera).*
>
> *Limited in-situ testing was available to assess adverse effects to aquatic receptors. Rotifer toxicity tests, which are logistically simple to perform, were conducted onboard ships and used as a decision tool during subsurface application of dispersants. However, these tests are considerably less sensitive than tests performed with early life stages of fish or crustaceans. Tests species amenable to field testing aboard ship aside from rototox should be explored in the near future.*
>
> *There were no studies on the photo-induced toxicity of chemically dispersed oil at the water surface. Studies should consider the increased toxicity of some PAHs in the presence of UV light by including exposures to natural sunlight or ultraviolet light. Also, most of the toxicity assessments conducted during the response were confined to PAHs (either total PAHs or comparisons versus benchmarks), and did not take into account other oil-related constituents (e.g., diesel range organics, normal alkanes, isoparaffins, heterocycles and unresolved complex mixtures) which may also contribute to the overall toxicity of dispersed oils.*

The group discussed the need for a database that incorporates biological effects for various species. The group recommends using proxy species to cover as many species as possible. Decision makers also need information on the resources at risk present in the affected ecosystem and their baseline conditions. Short-term response needs include real-time toxicity data, tracking the movement of contaminants and changes in concentration, understanding degradation products and their effects, and using a consistent approach to toxicity testing. From their discussions of decision makers' needs and R&D needs, the group developed a flow chart (Figure 2). The chart conveys the flow of information and how each step informs the next to ultimately establish useful tools for responders and knowledge on future spills. The group also developed the three priority R&D needs listed in Tables 10-12.

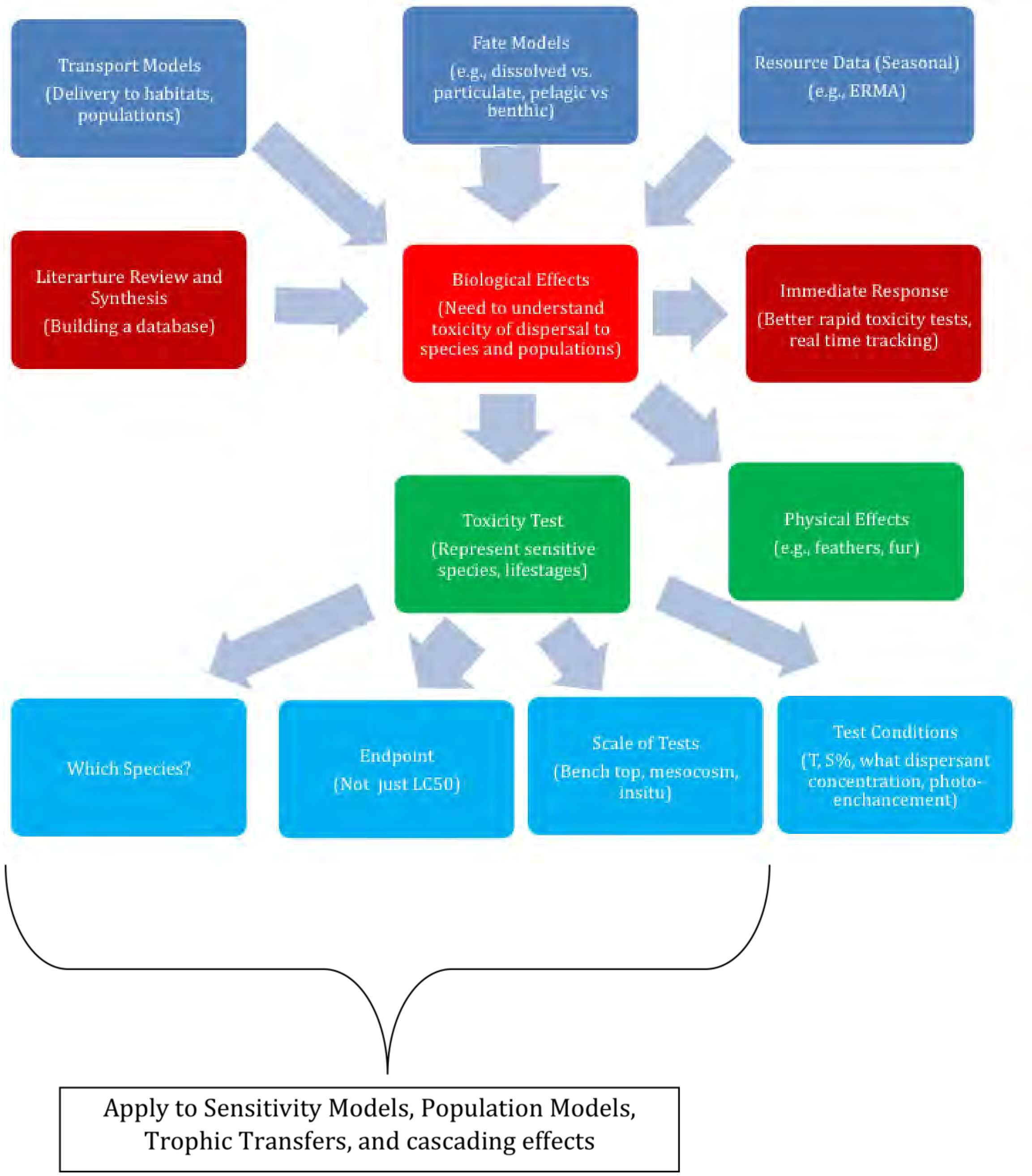

Figure 2: Flow chart conveying flow of information to establish biological effects

Table 10. Biological Effects of Dispersants and Dispersed Oil R&D Need Priority 1.

Research Topic	Identifying Resources at Risk to Dispersed Oil: Population Sensitivity Analyses
Objectives	Create an Ecosystem Consequence Analysis (ECA) that considers key populations at risk, recovery rates, and food web consequences, using Population Sensitivity Tables that inform many decisions (e.g., ecological to economic), identify data gaps and identify key species that drive tradeoff decisions
Guidelines	- Primarily a modeling approach - Use existing data to develop sensitivity tables and effects models
Issues/Problems	- Lack of data to make resource-based decisions - Understanding of long-term impacts
Application to Decision Making Process	Use of dispersants based on ecosystem consequences and tradeoffs.
Length of Time of Project	2-3 yrs
Total Cost Estimate	Medium, $300,000- $400,000

Table 11. Biological Effects of Dispersants and Dispersed Oil R&D Need Priority 2.

Research Topic	Developing a Systematic Process for Area-specific Biological Effects Assessments for Dispersant Use: Application to two contrasting environments (Cook Inlet, Alaska and Florida Keys, Florida)
Objectives	- Expand ERA process (transport, fate, receptors) to identify data gaps for determining area-specific biological effects of dispersed oil. Identify whether appropriate toxicity data using representative test conditions exist for resources at risk or their surrogates - Fill data gaps (additional information on transport, fate, resources, toxicity testing) to be able to apply results to decision making (including population models, trophic cascading effects). - Experimental validation at appropriate scales
Guidelines	
Issues/Problems	- Difficult to separate biological effects gap analysis from transport, fate, resources at risk - Every region has differing transport, fate, resources at risk
Application to Decision Making Process	Reduces uncertainty by providing relevant data
Length of Time of Project	>2 years
Total Cost Estimate	High, > $400,000

Table 12. Biological Effects of Dispersants and Dispersed Oil R&D Need Priority 3.

Research Topic	**Worldwide Compilation, Synthesis, and Analysis of Biological Effects from Dispersed Oil Under Controlled and Uncontrolled Oil Spills**
Objectives	- Data mining of peer review and gray literature of worldwide information and dispersant use in field laboratory, and accidental oil spills - Evaluate and analyze available data in scientifically rigorous process to extrapolate to relevant situations or decisions - Easily accessible, summarized, searchable (keywords: e.g., species, acute vs. chronic, characteristics), interactive and geo-referenced database on the effects of dispersant use - Initial report of findings with annual/biannual updates
Guidelines	Literature review of lab, field and real world monitoring
Issues/Problems	- Accessibility for database (e.g., publicly accessible) - Maintenance and continuing updates (how, who, when, where) - Training on database use (e.g., manual, on-site training) - Data may not be available (e.g., proprietary data)
Application to Decision Making Process	Informed tradeoff decisions based on past experiences Help identify risks and reduce uncertainty
Length of Time of Project	2 years
Total Cost Estimate	Medium, $100,000 - $400,000

IV e. Dispersants and Seafood Safety

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The following section includes excerpts from the biological effects white paper. The entire white paper can be found in Appendix 1e, including its references.

> *The aquatic toxicity of dispersant formulations has been examined and debated over many years. Following extensive reviews in 1989 and 2005, and suggested standardization of testing methods, dispersants in use today are generally reported to be less toxic than formulations prior to 1970 (e.g. NRC 1989, 2005, Fingas 2008). Corexit® dispersants in particular have been well studied with most reports indicating lower aquatic toxicity in direct comparisons with water soluble, water accomodated and chemically dispersed oil fractions (e.g., George-Ares and Clark, 2000; Liu et al., 2006; Judson et al., 2010; Hemmer et al., 2011). Other studies have addressed dispersant influence on the bioavailability and uptake of aromatic and*

aliphatic constituents of oil by various aquatic species (e.g. Milinkovitch et al., 2011; Jung et al. 2009; Mielbrecht et al., 2005; Fuller et al., 2004; Ramachandran et al., 2004; Cohen et al. 2001; Gagnon et al. 2000; Singer et al., 1998). However, the potential for dispersant constituents themselves to accumulate in aquatic species has received less attention. Several studies investigating uptake and disposition of principal dispersant constituents, ionic and nonionic surfactants, in aquatic species suggest rapid uptake, metabolic conjugation, concentration in liver and bile with transient enterohepatic circulation, and rapid elimination (Alvarez-Munoz et al., 2010; Tolls et al., 2000; Tolls & Sijm 1999; Goodrich et al., 1991; Granmo & Kollberg 1976; Calamari & Marchetti 1973). Distribution of surfactants into muscle tissues was reported to be low order and low BCF values for edible tissues. In one of few studies to assess the uptake and disposition of Corexit® constituent dioctyl sodium sulfosuccinate in aquatic species, Goodrich et al. (1991) noted rapid uptake and concentration in viscera and bile of rainbow trout, at significantly higher levels than uptake in either blood and carcass. BCFs were not determined for viscera or bile due to the lack of steady state conditions. BCFs of 3.47 and 3.78 were derived for blood and carcass compartments, respectively, indicating little bioconcentration in edible tissues.

The initial federal chemical safety assessment of Corexit® dispersants in the context of seafood safety included structure-activity modeling to estimate BCFs for Corexit® constituents. Consistent with existing information, predictive BCFs for Corexit® constituents, other than the nonionic surfactants and light petroleum distillates, fell below 10, suggesting low potentials for bioconcentration and accumulation in edible tissues of aquatic species. The BCFs for light petroleum distillate mixtures ranged from 60 to 80. Nonionic surfactant BCFs have been experimentally determined in fathead minnow with an average value of 39.6 and maximum value of 387, suggesting moderate potential for bioconcentration. However, high elimination rate constants indicated that these compounds are rapidly biotransformed in vivo are thus unlikely to accumulate in fish (Tolls et al., 2000). Dispersant concentrations in DWH surface applications at sea were estimated by the manufacturer to be approximately 30 μg/L in the area of the oil slick to a depth of 10 meters (Nalco, 2010). Previous research (Georges-Ares & Clark, 2000; NRC 1989) indicates that dispersant would be expected to be rapidly diluted and biodegraded in the ocean environment to levels below detection. Analyses for Corexit® constituents in surface water and sediment samples from the GOM after dispersant applications had ceased did not detect dispersant chemicals above limits of detection (EPA 2010b). However, deep subsurface sampling and analyses detected trace levels (12 ppb) of DOSS entrained in a hydrocarbon plume at 1000-1200 m water depth, suggesting slow to negligible degradation at depth (Kujawinski et al., 2011).

In considering the potential for chemical dispersants to compromise the safety of GOM seafood, initial questions concerned the potential toxicity of dispersant constituents, their concentrations, fate and persistence in the environment, their potential for bioconcentration in seafood species, and their disposition and persistence in seafood species. With the exception of dipropylene glycol monobutyl

> *ether, the constituents of Corexit® dispersants are recognized direct or indirect food additives under prescribed conditions of use. Corexit® dispersants used to treat the DWH oil spill were rapidly and extensively diluted in GOM waters, and environmental concentrations, estimated and measured, were commensurately low when detected. The physical-chemical characteristics and scientific literature indicate that dispersant constituents are susceptible to chemical and biological degradation, and that the potential for bioconcentration and persistence in the edible tissues of seafood species is low. The modeling, experimental, and field assessments performed during the response to the DWH oil spill, as well as the knowledge base accessed through scientific literature, indicated that Corexit® dispersants did not pose a threat to the safety of GOM seafood during or after their use. However, oil spills in different parts of the world differ in the nature and extent of public and environmental health hazards entailed, and consequently response strategies are rarely the same. There are numerous dispersant formulations available to responders, and in development for mitigation of oil spills under varying conditions. Future responders would benefit from a systematic assessment of all dispersant constituents, and their fate in aquatic species. A review of the existing knowledge base for dispersant constituents that are listed on the NCP product schedule should be performed to determine chemical makeup, environmental fate, kinetics, BCF/BAF, and potential human toxicity through direct or indirect exposure in order to identify constituents of potential public health concern. Some level of standardization of experimental designs informed by the needs of risk analysis, and testing methods for toxicologically valid markers of dispersant contamination in aquatic species would benefit risk managers and responders in the event of future oil spills.*

The seafood safety group identified three key decision makers' needs where information is not available or could be better understood. They are: (1) the need for sensory, analytical and extraction methods that have the ability to monitor concentrations of pollutants in seafood; (2) a better understanding of the chemical makeup, kinetics, toxicity, bioconcentration factor and bioaccumulation factor (BCF/BAF), environmental concentrations and levels of concern of dispersants (this information is known for COREXIT but needs to be established for all dispersant formulations); and (3) determination and summary of which state agencies regulate specific fisheries; for example, finfish and shellfish are often regulated by different groups. These three decision makers' needs lead to five prioritized R&D needs however, only the top three are shown in the tables below. For a complete list see the appendix.

Table 13. Dispersants and Seafood Safety R&D Need Priority 1.

Research Topic	**Conduct Literature Review**
Objectives	Conduct literature review of dispersant constituents for dispersants listed on the NCP product schedule to determine relevant information such as chemical makeup, environmental fate, kinetics, toxicity, bioconcentration factor, and bioaccumulation factor (BCF/BAF) in order to identify constituents of concerns or chemical markers
Guidelines	Secondary research, literature review
Issues/Problems	Proprietary issues related to formulations
Application to Decision Making Process	Direct
Length of Time of Project	< 1 year
Total Cost Estimate	Low, < $100,000

Table 14. Dispersants and Seafood Safety R&D Need Priority 2.

Research Topic	**Establish Standardized Experimental Design Criteria and Perform Environmental Fate, Kinetics, BCF/BAF Studies on Constituents of Concern**
Objectives	Determine likelihood of exposure from seafood consumption
Guidelines	- Consensus-based discussion Lab
Issues/Problems	- Developing consensus - Time and money
Application to Decision Making Process	Critical to feed into decision-making process
Length of Time of Project	>2 years
Total Cost Estimate	High, > $400,000

Table 15. Dispersants and Seafood Safety R&D Need Priority 3.

Research Topic	**Establish Standardized Experiment Design Criteria and Perform Mammalian Toxicity Studies on Constituents of Concern in order to Develop Reference Exposure and Risk Levels**
Objectives	Identify or develop reference exposure and risk levels
Guidelines	- Consensus-based discussion - Lab
Issues/Problems	- Developing consensus - Time and money
Application to Decision Making Process	Critical to feed into decision-making process
Length of Time of Project	>2 years
Total Cost Estimate	High, > $400,000

IV f. Dispersants and Human Health

Workshop Participants:
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Mike Fulton, NOAA Center for Coastal Environmental Health and Biomolecular Research
John Guarisco, Alabama Department of Public Health
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James Spahr, CDC The National Institute for Occupational Safety and Health
Mark Stenzel, National Institute for Environmental Health and Safety

The following section contains excerpts from the dispersant and human health white paper. Please refer to Appendix 1f for the full paper and references.

> *It will be a challenge to ascertain whether the application of oil dispersants into the Gulf of Mexico will have any perceptible effects on human health. The NIH-sponsored Gulf Long term Follow-up (GuLF) Study, led by NIEHS, is set to begin to study clean-up workers and volunteers to understand the scope and diversity of adverse health effects amongst those individuals most highly exposed to the toxic agents in question. One of its major challenges, however, will be to accurately characterize and quantify exposure to specific oil and dispersant chemicals alone, as well as in mixtures. Clearly, one of the prime issues will be to determine specific populations who were exposed to these agents and quantify the extent of their exposure in terms of time and amount. Detailed clean-up worker histories might allow grouping of workers based on their proximity in time and space to actual application of dispersants and comparing their ultimate health outcomes to oil clean-up workers with similar tasks in regions where dispersants were not applied. Clearly, a more accurate way to document exposure (an internal dose) would be to measure parent compounds or their metabolites in biological samples (blood, urine, other). However, the pathways of metabolism of DSS (dodecyl sodium sulphate) are not well described. Measurement of urinary 2-BAA has proven useful in monitoring employees potentially exposed to 2-BE in other settings70. It is important to remember, however, that these approaches are most useful only in the early stages following exposure since the compounds are presumably cleared fairly rapidly in the absence of a continuous exposure source. Moreover, there clearly are other sources of exposure for these agents such as laxative use and various household cleaning products containing glycol ethers. Therefore, for local residents not directly involved in clean-up activities, the background levels of exposure to many of these agents from other sources may approximate, or even exceed, those specifically from dispersant use. While biomarkers of effect would be useful, there are relatively few, if any, specific for these compounds. Measurement of RBC osmotic fragility could be used to monitor the hemolytic signature effect of E-series glycol ethers, but recall that*

humans are amongst the least sensitive species for this effect. Various measures of DNA damage and adduct formation in peripheral blood cells has provided some utility in measuring potential genotoxic effects after other oil spills.

The most fruitful future studies might be in regard to studying the interactions between oil dispersants and specific TPH components within the oil itself. Some chemicals in TPH might be more persistent than the dispersant chemicals so measurement of body burden with and without dispersant exposure might prove informative. Animal and in vitro studies that address availability and toxicity of TPH components in the presence and absence of dispersants should be carried out. For example, does simultaneous inclusion of dispersants in TPH component feeding studies alter the genotoxic and tumorgenic effects? Direct in vitro studies can easily be performed to determine if DSS or other oil dispersant components can increase permeation of oil components across skin. Human skin models employing cadaver-derived or tissue-engineered skin are routinely used to assess xenobiotic transport across this barrier in specifically-designed diffusion barrier chambers.

As pointed out earlier, the dispersant products themselves represent complex mixtures whose toxicity may not be adequately predicted by knowledge of the single ingredients alone. Few studies have directly tested the dispersant products for toxicity. Recently, the irritant and sensitizing properties of COREXIT 9500A and DSS were compared in a dermal application model in rats71. COREXIT was found to be about 10-fold more potent than would be expected based in its content of DSS alone. Acute 5 hr exposure of rats (27 mg/m3) of COREXIT aerosols was found to induce a small change in lung compliance without inflammation72 and changes in peripheral vascular reactivity73. These effects, however, were transient and extrapolation of the exposures conditions to those encountered in the real world is problematic.

The specific ingredients contained in many oil dispersant products remain proprietary information, however, those contained in COREXIT 9500 and COREXIT 9527, the products used almost exclusively in the Gulf, were available for review. Exposure of the general populace of Gulf shore to the major ingredients dioctyl sodium sulfosuccinate, 2-butoxyethanol, propylene glycol butyl ether, and other ethoxylated alcohols should be considerably below the range expected to produce adverse effects based on a review of their toxicological profiles. Of note, however, is the severe paucity of both human and laboratory data regarding the potential effects of chemical mixtures as represented by oil dispersant products. Those individuals involved in clean-up operations that directly handled oil dispersants or worked in the immediate area of application probably encountered greater amounts of dispersants and might a greater risk of adverse effects, but, in general these should be mild and self-limiting. Importantly, for several of the major toxicities described in experimental animals, humans appear to be comparatively resistant. Perhaps a greater question pertains to the ability of dispersants to alter the toxicological properties of the chemicals contained in the oil itself. By their nature they are designed to alter the fate and transport of crude petroleum and its constituents and, *therefore, can change the route and extent of human exposures. The physico-chemical properties of petroleum hydrocarbons contained in micro- -sized oil droplets desperately needs to evaluated and compared to petroleum hydrocarbons alone, in simple aqueous solution, and in air. Moreover, some the oil dispersant products themselves have potential to directly modify biological barriers and, thus, alter permeation of oil-derived chemicals at various routes of exposure.*

The human health breakout group developed a large list of decision maker needs regarding dispersants and human health; this list is included in the appendix. The key needs are: establishing factual information synthesis (e.g., dispersant components, understanding effects, worker safety), establishing hazard identification and exposure scenarios, understanding risk to workers and public safety, and communicating the risk successfully, and understanding the trade offs of using dispersants with respect to human health. There were three priority R&D needs (Tables 16-18).

Table 16. Dispersants and Human Health R&D Need Priority 1.

Research Topic	**Toxicological Effects**
Objectives	- Determine the biological effects in mammalian systems of dispersant oil/mixtures and compare to those predicted or measured by exposure to individual components alone - Dispersants vs. ingredients - Oil vs. dispersed oil - Acute, repeat, longer term exposures - Target pulmonary, cardiovascular, central nervous system (CNS), and immune response - Synergistic and additive effects - Better characterization of toxicological profiles of additional dispersant products in mammalian models -Develop an understanding the biological effects (health hazards) of the dispersants as a formulation and a target agent (oil) - Determine the short- and long-term human health impacts from various routes and ranges of exposure for each dispersant that is available for use - Can standardized animal in vitro or in silico models be developed or can the toxic effects for human health be evaluated
Guidelines	- Laboratory - Models
Issues/Problems	- Proprietary information - Selection of the appropriate model and endpoint - Formulations of oil, dispersants and/or mixtures
Application to Decision Making Process	- Accurate for hazard identification - Proof of principle - Importance of mixtures - Maintain an appropriate schedule of dispersants - Criteria for selection for a safe and effective dispersant - Better incorporation of safety data
Length of Time of Project	Various, depends on scope
Total Cost Estimate	High, > $400,000

Table 17. Dispersants and Human Health R&D Need Priority 2.

Research Topic	Exposure
Objectives	- Measure or develop models to estimate exposure to dispersants and or dispersed oil to human populations - Occupational - Resident - Develop an upper bound of exposure of the variable exposure scenarios associated with the dispersant use - Environmental - Occupational
Guidelines	- Lab - Field
Issues/Problems	Access or gather existing information
Application to Decision Making Process	- Exposure control, potentially operational decision-making, risk communication
Length of Time of Project	1-2 years
Total Cost Estimate	Medium, $100,000 - $400,000

Table 18. Dispersants and Human Health R&D Need Priority 3.

Research Topic	Epidemiology
Objectives	- Study the health effects in known potentially exposed human populations (dispersant manufacturing and response and remediation application). - Develop relevant biological markers of exposure and guidelines for responsible use of the biomarker
Guidelines	- Lab - Field based exercise
Issues/Problems	- Dealing with humans - Identification of sufficiently large exposed population - Appropriate controls - Validation of relevant biomarker
Application to Decision Making Process	- Human health risk assessment - Potential bio-monitoring
Length of Time of Project	>2 years
Total Cost Estimate	High, > $400,000 (could be millions)

IV g. Dispersants and Risk Communication

Workshop Participants:
Group Lead: Ann Hayward Walker, SEA Consulting Group
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Ed Levine, NOAA Office of Response and Restoration
Steve Picou, University of South Alabama
Lisa Symons, NOAA Office of National Marine Sanctuaries

The following section contains excerpts from the dispersant and risk communication white paper. The entire white paper can be found in Appendix 1g.

> *Risk communications is a research area of the social sciences which is closely associated with human dimensions and external communications. External communications, traditionally in the purview of public affairs, may have multiple purposes including influencing public beliefs, opinions, and judgments about the incident. Risk communications on the other hand:*
>
> - *Includes actions, words, and other interactions that incorporate and respect the perceptions of the information recipients, intended to help people make more informed decisions about threats to their health and safety (Ropeik, 2008).*
> - *Ropeik, D. 2008. Risk Communication: More Than Facts and Feelings. International Atomic Energy Commission Bulletin. 50-1:58-60.*
> - *Is the interactive process of exchange of information and opinions among individuals, groups, and institutions concerning a risk or potential risk to human health or the environment. (National Research Council, 1989) National Research Council, Committee on Risk Perception and Communication. Improving Risk Communication. National Academy Press, Washington, DC. 1989.*
> - *Means communication intended to supply lay people with the information they need to make informed, independent judgments about risks to health, safety and the environment. (Morgan et al 2001) Morgan, M.G., B. Fishoff, A. Bostrom and C.J. Atman. 2001. Risk Communication: A Mental Models Approach. Cambridge: Cambridge University Press.*
>
> *There are many approaches toward risk communications. Some of them focus on improving the way external communications about risks are conducted, e.g., developing better messages, and some focus on the content of risk communications, that is, sharing technical information to support the assessment of the potential for risks. Better messages, engagement, and risk-based communications were needed during DWH.*

To provide some background, the extended quote below from a 1993 EPA document (Use of Chemical Dispersants for Marine Oil Spills), reveals the fact that practical considerations for dispersant use have historically been complex and contentious:

> *During an oil spill, a confluence of competing interests must be balanced. The news media likely will be on the scene requesting statements on any action that is being taken to respond to a spill event. Various interested parties such as representatives of the vessel owner, the cargo owner, local fishing interests, businesses dependant on tourism, local/state/federal government agencies, environmental organizations, equipment vendors, and cleanup companies will appear on the scene and advocate their position to both the OSC and the press. Often the various groups approach spill response from a different base with different objectives. Decision making, management, and organization of a spill response are made more difficult by maintaining open communication with the various interest groups; but eventually the effort to maintain the interaction and develop it organizationally can result in a much more effective response. Management and organization of oil spill responses have been studied (Cohn et al, 1991; Noble, 1991), but there are no tested paradigms that account for the rapid action and public input required in a crisis situation.*
>
> *With the multitude of problems that can arise in the U.S. legal environment and the strong antipathy toward the use of dispersants that has developed among some interested parties, the OSC should reflect carefully on dispersant use and be ready for criticism. Two considerations guide the decision-making process affecting an actual dispersant use situation:*
>
> - *There is a reasonable probability of measureable success (e.g., preventing oil from reaching a beach or breeding area).*
> - *Consensus agreement has been reached between potentially affected parties that dispersant application is worthy of being evaluated as a response.*
>
> *Measureable success, even if it is not complete, will vindicate the decision to use a dispersant. Although it may not be required, a consensus agreement will help to defuse critics who challenge a response that does not achieve success. Numerous other considerations will come into play in a response involving the prospect or the actual use of dispersants. It is beyond the scope of this document to attempt to identify all of the possibilities. The final decision will be based on the experience, understanding, and knowledge of the decision makers and their risk tolerance.*

At the Deep Water Horizon (DWH) response there was some degree of measurable success, however, the consensus agreement in place prior to the spill was superseded by the magnitude of the spill and subsequent large amount of dispersants applied. The breakdown of consensus among government agencies, (e.g., when the state of LA abstained in its vote for dispersant use and the EPA began requiring additional testing and limitations) contributed to public concern regarding the use of dispersants.

There were multiple efforts to inform the public about the necessity to use dispersants during the response to the DWH spill. The Public Affairs and Liaison Units in conjunction with the Environmental Unit (EU) prepared numerous press releases, public information brochures, posters, talking points, graphics, and statements. The objective of these activities were to inform the media and general public on the reasons dispersants were being used, the rationale behind the decisions, the efforts to monitor the applications, and the successes that were achieved.

From the vantage point of the command post, it appeared that the messages were being received in the fashion that they were intended. Early in the incident several people came from Alaska to talk with the fishing communities about their experiences during the Exxon Valdez spill, in the interest of helping Gulf communities prepare for what to expect. An important assumption was made prematurely that the two spills, and therefore the effects, were very similar and that the Gulf experience would closely parallel the Alaska experience. Some significant differences in the two spills were not acknowledged (e.g., locale, environment, oil, etc.). As a result of these interactions, some people in the community, including fishermen, developed negative sentiments toward dispersant applications or the addition of "chemicals." The Alaskan visitors to the Gulf spoke of people getting ill and fish dying. The Unified Command staff in the command post was not pro-active enough to get ahead of the negative stories being promulgated. The media took the sensationalism of the 20-year-old Exxon Valdez saga and retold them to larger audiences. Many examples of the ecological and social consequences of the Exxon Valdez spill were supported by peer reviewed journal articles and research funded by recognized agencies such as the National Science Foundation (Rice. 2009; Picou. 2009). However, combined with claims of health impacts, the resulting media accounts led to a confusing assortment of information that resulted in a "media scare" and increased anxiety for residents along the Gulf of Mexico.

Lingering Issues

- *Questions related to this topic that were resolved during DWH:*
  - *Is it possible to mount a coordinated large-scale dispersant operation?*
  - *Can you monitor dispersant effectiveness?*
  - *Was the public affairs unit prepared for communicating risks from dispersants to the public and other stakeholders?*

- *Knowledge gaps and questions that remained unresolved by DWH:*

  - *How much is too much?*
  - *What are the effects on sea life?*
  - *How long do dispersants remain in the environment?*

- *New questions that resulted from DWH relative to the topic:*
  - *How do you explain the issues involved in tradeoffs?*
  - *How do you build a trusting relationship after a disaster occurs?*
  - *What are some products that contain similar chemicals to dispersants that people can relate to?*
  - *How do you maintain, or rebuild, public confidence in seafood safety?*

- *R&D needed to resolve outstanding questions relative to topic:*
  - *How can you monitor for effectiveness in a more real-time mode and translate the results to risk communications for public health and safety?*
  - *How can you build shared values during a spill response?*
  - *How do you plan for and recognized the human dimensions of oils spills?*

The risk communication breakout group compiled a detailed list of decision maker needs. The key needs are: establishing a link between technical specialists and agency officials, understanding what various agencies need to communicate at different levels to stakeholders (e.g., federal, state, local), establishing method for communicating accurately and succinctly a description of a net environmental benefit analysis (NEBA), setting reasonable expectations at the forefront of a spill, and informing the scientific community about spill response structure and framework. The three R&D needs the group developed are shown in Tables 19-21.

Table 19. Dispersants and Risk Communication R&D Need Priority 1.

Research Topic	**Conduct a Needs Assessment Study (Survey) of External Stakeholders for Spill Response Literacy, Dispersant Information Needs and Expectations and Recommendations for Future Preparedness and Response**
Objectives	Supply laypeople (political/elected officials/general public/local stakeholders) with credible information they need to make informed judgments about risk to health, safety, and environmental tradeoffs associated with oil spill response including dispersant application
Guidelines	Identify what the information needs are based on stakeholder group perspective (culturally sensitive) and develop recommendations for mechanisms to meet these information needs and expectations using multiple research methods (e.g., focus groups, surveys, structured interviews)
Issues/Problems	Acknowledge external (general public) stakeholder perception that unified command inherently involves a conflict of interest (e.g., transparency on the release of proprietary ingredients)
Application to Decision Making Process	Yes
Length of Time of Project	2 year
Total Cost Estimate	High, > $400,000

Table 20. Dispersants and Risk Communication R&D Need Priority 2.

Research Topic	**Research Methods to Effectively Communicate, Educate Stakeholder Groups (General Public) with regard to Dispersants and Oil Spills, Environmental Trade-Offs, Human Health and Seafood Safety Issues**
Objectives	- Identify specific content and delivery channels and mechanisms for providing additional information for internal and external stakeholders - Translate scientific issues relating to oil spills, spill technologies, and dispersants into something tangible for the general public thereby narrowing the gap
Guidelines	- Field applications including nominal group processes, two-way exchange - Intent is for research topic 1 to inform research topic 2
Issues/Problems	- Overcome barriers of stove piping specialized knowledge - Topic cuts across multiple issue topics - Solutions and products will need to be maintained/updated/revisited periodically - Need to re-evaluate periodically (e.g., every 5 years) - Cultural/geographic sensitivities
Application to Decision Making Process	Fosters interagency and scientific collaboration
Length of Time of Project	2 years or more
Total Cost Estimate	High, > $400,000

Table 21. Dispersants and Risk Communication R&D Need Priority 3.

Research Topic	**Regional perceptions of spill response, dispersants and seafood safety**
Objectives	To determine attitudes and behaviors relative to consumption of seafood in restaurants and household purchases
Guidelines	Field study
Issues/Problems	Address the continuing consumer fear of GOM seafood
Application to Decision Making Process	Provide information to target communication of seafood testing and monitoring to reluctant consumers and inform local seafood associations
Length of Time of Project	1 year
Total Cost Estimate	Medium, $100,000 – $400,000

V. Synthesis, Next Steps, Recommendations

On the final day of the workshop, seven new groups were assigned mixing the topic groups and responders and researchers. Each of these new groups decided on seven high priority R&D needs from the list of R&D needs developed in the previous two days. Of these top needs, two were common among all groups, two were identified by six of seven groups, and one was identified by five of seven groups. Hence, five R&D needs were seen as priorities among the vast majority of participants. These five R&D needs in order of priority are:

- Develop and implement a research program on quantification of degradation rates of chemically dispersed, physically dispersed, and undispersed oil (see Table 5)

- Develop innovative analytical techniques to improve surface and subsurface dispersant response activities (application, monitoring of effectiveness to support decision making, and real-time data reporting) (see Table 3)

- Develop research methods to effectively communicate and educate stakeholder groups and the general public on dispersants and oil spills, environmental trade-offs, human health, and seafood safety issues (see Table 20)

- Investigate subsea dispersant application, including what are likely the most effective dispersants for subsea consideration, when should they be used, what are the most effective application methods and rates, and how to predict/measure effectiveness (see Table 2)

- Identify resources at risk to dispersed oil using population sensitivity and ecosystem consequence analyses that consider key populations at risk, recovery rates, food web consequences, using population sensitivity assessment that inform many decisions (e.g., ecological to economic), identify data gaps, and identify key species that drive tradeoff decisions (see Table 10)

Previous efforts have identified R&D needs for dispersant use and reached similar outcomes. The 2005 National Research Council (NRC) Oil Spill Dispersants: Efficacy and Effects report includes a discussion on R&D needs, and the subsequent CRRC workshop in 2005 brought together experts with various perspectives to reach consensus on the highest priority R&D needs to improve our understanding of dispersant use and its effects. In September 2010, the Joint Industry Oil Spill Preparedness and Response Task Force (JITF) published a report including their recommendations to improve oil spill response and preparedness, including dispersants. In November 2011, the JITF published a progress report and additional recommendations. Table 22 compiles these previous identified R&D needs.

Table 22. Recommendations for dispersant R&D from 2005 NRC Report, 2005 - present CRRC efforts, and the September 2010/November 2011 JITF Oil Spill Response reports.

Recommendations	Source
Efficacy and Effectiveness	
Develop and implement focused series studies to better predict the effectiveness of dispersants for different oil types and environmental conditions based on climatological data supplemented with real-time *in situ* observations	NRC, 2005
Experimental systems used for bench-scale effectiveness tests should: 1) determine the energy dissipation rates that prevail over a wide range of operating conditions; 2) measure chemical effectiveness over a range of energy dissipation rates to characterize the relationship between these variables; and 3) include measurement of the droplet-size distribution of the dispersed oil.	
Oil trajectory and fate models used during spill response to predict the behavior of dispersed oil should be improved, verified, and validated in an appropriately designed experimental setting or during actual spills	
Initiate a detailed investigation of wave-tank studies that specifically address the chemical treatment of weathered oil emulsions	
Initiate a detailed investigation of upper sea-surface turbulence with particular emphasis on quantifying horizontal and vertical diffusivities and the rate of energy dissipation	
Conduct the following studies on subsea injection: · Develop a summary of how subsea injection was utilized during the DWH response. · Develop a program for modeling and scaled testing of subsea dispersant injection to develop implementation criteria. · Investigate whether non-solvent based dispersants can be used effectively with this application mode due to rapid and uniform testing. · Work in conjunction with the Marine Well Containment Task Force to develop more efficient methods of applying the dispersants	JITF, 2011
Sponsor selected research projects in subsea application	
Review surface application techniques and capture learnings from the operational teams of DWH and sustain and enhance targeting and application capabilities learned	

Recommendations	Source
Fate and Effects	
Develop and fund focused series studies to quantify the weathering rates and final fate of chemically dispersed oil droplets compared with undispersed oil	NRC, 2005
Initiate a detailed investigation on the kinetics of dispersed oil biodegradation at low oil-water ratios to simulate conditions that represent those that follow significant dilution of the dispersed oil plume. Droplet-scale models of biodegradation kinetics should be developed and the appropriate kinetic parameters should be estimated. Biotransformation products of high-molecular-weight PAH should be investigated using indigenous microbial communities from seawater	
Develop and fund focused toxicity studies to determine the mechanisms of both acute and sublethal toxicity to key organisms from exposure to dispersed oil.	
Develop and implement steps to ensure that future wave-tank or spill-of-opportunity studies implement a field program to measure both dissolved-phase PAH and particulate/oil-droplet phase PAH concentrations for comparison to PAH thresholds measured in toxicity tests and predicted by computer models for oil spill fate and behavior	
Develop and implement focused toxicity studies to: (1) provide data that can be used to parameterize models to predict photo-enhanced toxicity; (2) estimate the relative contribution of dissolved and particulate oil phases to toxicity with representative species, including sensitive species and life stages; and (3) expand toxicity tests to include an evaluation of delayed effects.	
Provide cross-training of modelers and scientists in disciplines of physical, toxicological, and population models so that they jointly agree on necessary standards; identify additional research needed to improve models	CRRC, 2005
Review data collection efforts for spill impact assessment and evaluation of ecological recovery rates for offshore, near-shore, coastal and estuarine areas impacted by spills.	JITF, 2010
Development of remote “survey” technologies for rapid and accurate detection of oil and plumes in deep- and mid-water over larger distances	
Development of fine-scale plume sampling and analytical methodologies that accurately characterize the plume, e.g. Polycyclic Aromatic Hydrocarbon (PAH), TPH, water-accommodated fraction, with respect to chemical constituents of concern that are directly relevant for ecological risk assessments	
Sponsor selected research projects on ecotoxicity and biodegradation, and oil and dispersant fate and behavior from deepwater releases	JITF, 2011

Recommendations	Source
Other	
Develop and implement detailed plans (including pre-positioning of sufficient equipment and human resources) for rapid deployment of a well-designed monitoring effort for actual dispersant applications in the United States	NRC, 2005
Identify data gaps and weaknesses in existing protocols; update existing protocols to incorporate new technologies; extend use of results through distribution via accessible databases/websites	CRRC, 2005
Provide cross-training of modelers and scientists in disciplines of physical, toxicological, and population models so that they jointly agree on necessary standards; identify additional research needed to improve models	
Improve operational monitoring at spills to be able to document spatial and temporal concentrations of dispersed oil (dissolved and particulate)	
Develop a response guidebook that would provide guidance for oil spill and hazardous material response. This guidebook should address: 1) establishment of proper communication channels; 2) descriptions of common data management schemes that promote data sharing; 3) resource management; 4) guidance on setting response priorities; 5) procedural information for funding the assessment; 6) guidance on the assessment process for determining the types of debris and who is responsible for removal; 7) guidance on assessment and plan development for handling dangerous wildlife and pets; and 8) plans for rapid training for response workers and volunteers	CRRC, 2009
Develop a series of simple fact sheets and/or other communication tools addressing various aspects of dispersants (effectiveness, tradeoffs, safety & health aspects, applicability in low wave environments and near-shore).	JITF, 2010
Industry will sponsor an Industry-government (EPA; USCG; NOAA; etc.) workshop to discuss ways to improve dispersant decision making and use, including: · ACP process for tiered thresholds/approvals for dispersant use. · Review and discuss the rationale for stockpiling certain approved dispersants and consider adjusting the make-up of future to stockpiles as appropriate. · Review potential options to change regulatory procedures to allow a process for interim EPA approval for, under emergency situations, the use of dispersants that are stockpiled by response agencies outside of the US. · Effectiveness monitoring protocols for surface (i.e. Special Monitoring of Applied Response Technologies (SMART)) and subsurface application.	JITF, 2011

All topic groups (original seven groups) discussed risk communication or scientific literacy as a major area for improvement. Communication to the public, as well as to federal, state and local agencies was seen as one of the largest issues during DWH. There has been very little funding in this area with respect to oil spills in the past. The outcome of this initiative clearly demonstrates a need for further research in risk communication and oil spill response and restoration. Another key area discussed among numerous groups, was the need to develop a system for incorporating ecosystem consequence analyses (ECA) into the decision making process and expanding the environmental risk assessment (ERA) process to include toxicity data. It is recommended that a retrospective net environmental benefit analysis (NEBA) be conducted on the DWH in order to inform future dispersant use. One final significant information gap is the understanding of dispersant oil interaction, transport, and fate in the subsurface. Further research into dispersant application in the subsurface and its effects are recommended. Responders to future spills may consider subsea dispersant use again, so it is crucial that they have a better understanding of when and how to apply them. If there were a spill tomorrow and dispersants were an option, decision makers and responders need to be prepared to properly communicate and defend their decisions, in order to accomplish this some key information gaps need to be filled. The ongoing research funded by the Gulf Research Initiative and some industry funded work are targeting these gaps; however, it will take a coordinated and broad effort incorporating federal and state agencies and international partners to accomplish the goals set forth by this initiative.

This initiative and all of its outcomes will help CRRC and NOAA develop a research plan to address the most pertinent research needs that will fill information gaps and provide a better understanding of dispersants to make informed, scientifically-driven decisions regarding dispersant use in future oil spills.

APPENDICES

The Future of Dispersant Use in Oil Spill Response Initiative

Coastal Response Research Center

Research Planning Incorporated

National Oceanic and Atmospheric Administration

Coastal Response Research Center

APPENDICES

1. Unabridged White Papers
    a. Dispersant Efficacy and Effectiveness
    b. Degradation of Dispersants and Dispersed Oil
    c. Physical Transport and Chemical Behavior of Dispersed Oil
    d. Biological Effects of Dispersants and Dispersed Oil on Surface and Deep Ocean Species
    e. Dispersant and Seafood Safety
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Dispersant Efficacy and Effectiveness

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Introduction

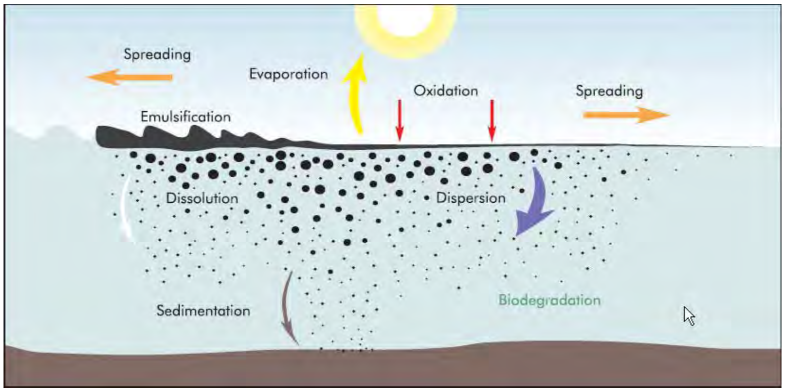
Dispersants have been researched extensively and used for oil spill mitigation for more than 40 years, yet there are opportunities to enhance our understanding, including with respect to their long term fate and effects and how to optimize dispersant use. For example, the 2005 National Academy of Sciences report, *Understanding Oil Spill Dispersants: Efficacy and Effects*, suggested a number of areas where increased understanding would help support the use of dispersants. Throughout the summer of 2010 dispersants were used in unprecedented quantities and, in the case of sub-sea application, with novel application methods following the Deepwater Horizon incident. The focus of this paper is to provide a brief overview of spilled oil behavior, chemical dispersants efficacy and effectiveness, and a discussion of the state of knowledge pre-, during, and post- Deepwater Horizon.

Oil Behavior

After oil is spilled, it typically undergoes eight main fate and weathering processes (Figure 1), which may all occur simultaneously in different degrees:[1]

1. Spreading and advection
2. Evaporation
3. Dissolution
4. Dispersion
5. Emulsification
6. Photo-oxidation
7. Sedimentation and shoreline stranding
8. Biodegradation

Figure 1 – Processes Acting on Spilled Oil (ITOPF)[2]



Dispersant Overview

Natural dispersion of oil into water can be enhanced through the application of dispersants, either at the water surface by aerial or vessel spray application or by using subsea injection at the source of a subsea spill. The primary objectives of dispersant use are to reduce environmental impacts associated with surface slicks (e.g., impacts to marine mammals, seabirds, marshes, etc.), enhance removal of oil from the environment through biodegradation, and rapidly reduce toxicity through dilution.

The overall effectiveness of oil dispersion has three components:[3]

1. Operational effectiveness, which describes how well dispersant is applied and incorporated into the released oil
2. Chemical effectiveness, which describes the fraction of treated oil that is entrained as small droplets in the water column
3. Hydrodynamic effectiveness, which describes the transport of the chemically dispersed oil plume and its dilution by turbulent diffusion through horizontal and vertical mixing processes

One of the primary benefits of using dispersants is that they are not nearly as limited by natural conditions/processes as mechanical recovery and *in situ* burning. While booms begin to lose effectiveness in wave heights greater than 1 m (3 feet), dispersants are in fact more effective as mixing energy (e.g., wave energy) increases. The upper wave-height limit for dispersant application is typically defined by personnel safety concerns caused by high winds and rough seas. However, for low-viscosity oils that have not weathered and emulsified, natural dispersion (i.e., dispersion without using dispersants) will quickly remove oil from the surface when waves exceed 3 m (10 feet)[4].

Further, dispersants can be applied from airplanes and helicopters in addition to vessel application, allowing for rapid deployment over long distances and rapid treatment of large areas. Both mechanical recovery and *in situ* burning are limited to boat-based operations, which means relatively slow transit times and even slower operational speeds because of their reliance on boom-based systems, which leads to lower encounter rates with the oil. In the case of vessel-mounted dispersant spray systems both large and small vessels may be used, offering a level of flexibility with respect range of operation (see Figure 2, for example). When one considers that, from a risk perspective, small and medium spills happen more frequently, the use of vessels may offer an effective dispersant response. For example, in Norway, contingency plans that include the use of dispersants are based on the analysis of various scenarios, including those from spills of less than 100 m^3 (625 bbl, 26,250 gal).

Figure 2 - Example of Large Scale Vessel-Mounted Dispersant Spray System

Photo courtesy of Sintef

As a result, the use of dispersants during an oil spill, both surface and, more recently, subsurface, is a critical element in reducing the size and duration of surface slicks and in preventing significant oiling of sensitive shoreline habitats. During the Deepwater Horizon incident, subsurface dispersants were also used to keep oil from surfacing near the well site. This eliminated potential health and safety risks to well-control personnel from volatile hydrocarbon vapors.

While dispersant use has many advantages, it has raised concerns in the media for example, long-term effects on human health, seafood, wildlife, and ecosystems. Key advantages of dispersants are summarized as follows:

- Dispersants can be used over a wider range of environmental / meteorological / oceanographic conditions than other response options. They can be applied in rough seas (up to 3 m) and on thinner oil slicks (<<1 mm). Furthermore, subsea injection of dispersants may have even fewer restrictions since it can proceed 24 hours per day and is less susceptible to weather conditions at the surface. Modern sensing technologies (e.g., aircraft fitted with real time down link transfer of forward looking infra-red video (FLIR- video) offer the possibility of night time operation of spray vessels as well.[5]

- Dispersants can treat much more oil over time than other response options. They can be applied at high speeds by aircraft. In addition, aircraft allow for rapid transit to a spill location and relocation to slicks separated by significant distances. Modern vessel-based application could potentially be a primary strategy, especially in those areas supply/response vessels are fitted with spray systems, large capacity storage, and state of the art high and low dosage spray systems for added response flexibility, especially as windrows and other less homogeneous slicks form. In addition to these well established methods of dispersant use, , the use of subsea dispersant injection can continuously treat all oil at the source before it spreads over a large area at the surface.

- Dispersants reverse, stop, or eliminate water-in-oil emulsion formation particularly when applied to low-viscosity oils. Emulsions can become very stable and a challenge to treat with any response option. If emulsions form, the potential for oils to reach shorelines increases.

- Dispersants accelerate the biodegradation of oil by decreasing droplet size and thereby increasing the amount of oil surface area available to bacteria. In addition, rapid dilution of dispersed oil ensures that biological activity does not exhaust available nitrogen, phosphorous, and oxygen needed for biodegradation.

- Subsea injection of dispersant reduces the amount of oil coming to the surface and this in turn (a) reduces the potential for exposure of surface vessels and personnel to volatile components of the oil and (b) reduces the need for surface recovery, *in situ* burn, and surface dispersant operations, thereby reducing a variety of safety risks for response personnel potentially involved with these operations. Surface application of dispersants in the vicinity of well containment operations can also reduce the potential for personnel exposure to volatile oil components.

Dispersant use often transfers oil into the water column increasing its probability for reaching subsurface marine organisms that might not otherwise be exposed to oil. Other concerns with dispersant use include:

- Dispersants in oil may reduce the performance of oleophilic skimmers, which rely on the adhesive properties of oil. There have been a few suggestions that the effect of residual surfactants on oil adhesion may reduce the efficiency of this type of skimmer although there is little supporting evidence for this, in fact, experience in Norway indicates that an increase in efficiency may be obtained in some instances. [6]

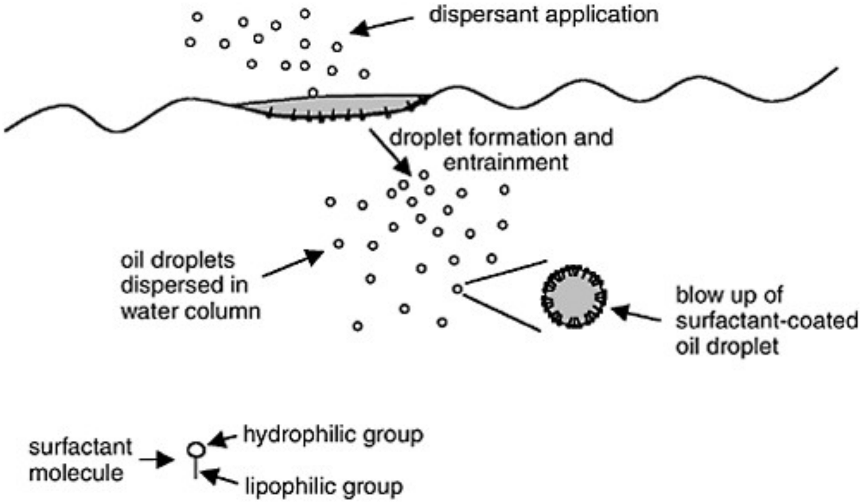
- Dispersants are not universally effective on all types of oil. Higher viscosity oils, oils that have weathered and become more viscous, oils that have cooled significantly below their pour point, and oils that have emulsified are less dispersible than light, low-viscosity oils. Empirical studies have shown that oils with pour points up to 10-15° C higher than the sea temperature may still be chemically dispersed.[7] However, current research has focused on dispersants that are formulated to work on heavy and weathered oils.

- Dispersant use on patchy slicks can be inefficient when applied by large fixed wing aircraft. For example, a large C-130 plane may have a swath width significantly greater than the width of slicks after they line up in relatively narrow windrows over time. This inefficiency can be addressed by applying dispersants to these slicks by boat to avoid spray drift or smaller aircraft with more appropriate swath width.

Mechanism of Chemical Dispersion

Modern dispersant formulations facilitate natural processes that remove oil from the environment through biodegradation. They are mainly composed of surfactants that reduce interfacial tension between oil and water to allow the formation of micron-sized droplets of oil that are entrained into the water column by wave energy (Figure 3). For comparison, without dispersants, thick oil slicks generate millimeter-sized droplets when impacted by waves. These larger droplets tend to rapidly rise back to the surface where they coalesce and reform the slick. The smaller droplets (e.g., 70 microns) formed after applying dispersants remain in the water column and become a concentrated energy source for oil-degrading bacteria. Marine environments around the world contain oil degrading bacteria that have evolved to consume oil released by natural seeps.[8,9]

Figure 3 – Mechanism of Chemical Dispersion (National Research Council)[4]



A misperception about dispersants is that they cause oil droplets to rapidly sink to the seabed. This is not the case since dispersants are less dense than sea water and dispersed oil droplets remain positively buoyant *unless* they encounter and associate with heavier marine sediments or lose significant amounts of their lighter components via dissolution, evaporation or degradation. In marine waters far from shore, encountering enough sediment to rapidly sink large quantities of dispersed oil is unlikely. The droplets generated after applying dispersants range in size from a few microns up to 100 microns in diameter. The rise velocities of these droplets are insignificant compared to the turbulence found in the open ocean. If these droplets become negatively buoyant through degradation or dissolution, they would be even smaller with very low fall velocities. The end result is that once dispersed oil enters the water column, it tends to remain entrained without resurfacing or falling to the seabed until it is removed from the environment through biodegradation.

Efficacy

A significant amount of research shows that low-viscosity oils, disperse even after significant weathering and at cold temperatures.[10,11,12,13,14,15] Other research has shown nearly complete dispersion during wave-basin tests of several low viscosity Alaska North Slope crude oils.[16] However, dispersant effectiveness tests provide conflicting evidence of the benefits of using dispersants under low-energy conditions and for water-in-oil emulsions because lab and basin tests can result in highly understated estimates of field effectiveness, i.e., lab test efficacy results may not be completely representative of real world dispersant effectiveness. Even in the case of the largest outdoor test tanks, oil spreading is constrained and dispersant effectiveness may be underestimated as a result (Figure 4).

Figure 4 – Large Wave Basins Constrain Slick Spreading

Photo of the BOEMRE OHMSETT (Leonardo, NJ) Test tank courtesy of TS Coolbaugh

Effectiveness tests are performed to determine if a dispersant can disperse a specific type of oil. These tests are conducted in closed systems, e.g., lab beakers or large wave basins, and for short durations, i.e., from a couple of minutes for some lab tests to 30 minutes for some wave-basin tests. Although it takes time, oil can spread to an extremely thin layer at sea, whereas beakers and basins keep oil artificially thick by limiting its natural tendency to spread. Constraining both time and surface area in dispersant efficacy tests can lead to underestimation of effectiveness because a) more viscous oils such as weathered crudes or water-in-oil emulsions take more than a few minutes to disperse and, b) thin oils disperse more easily than thick oils. In low-energy conditions, the dispersion process can take longer as well because oils must spread thinner before they disperse.

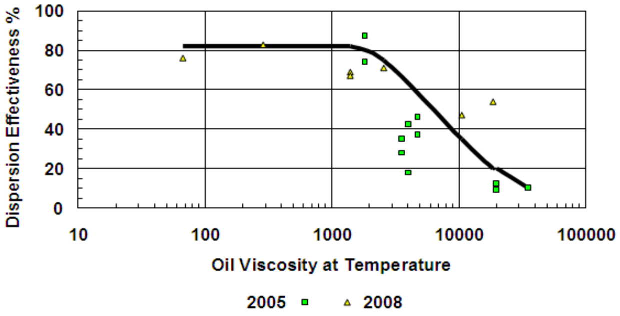
Currently six basic laboratory efficacy tests are routinely employed to evaluate the performance of dispersants. [17] Each test method has its own distinct characteristics and care should be taken to when comparing results between them. While the numerical results of these tests are useful for comparing dispersants on a relative basis, they may not be representative of actual performance expected at sea; clearly there is room for harmonizing testing methodologies.

Viscosity Effects

Unfortunately, recent literature on dispersant effectiveness can be misleading. The goal of a large percentage of recent research on dispersants has been to determine the operational limits for viscous crude oils and emulsions. But, as indicated above, many viscous crudes and emulsions may not rapidly disperse in wave basins and beakers. In contrast, a light crude oil, like the ~35°API gravity* crude spilled during the Deepwater Horizon incident, can be easily dispersed. The fact that recent literature has focused on oils that are difficult to disperse leads to the erroneous conclusion that dispersants sometimes work and sometimes do not. This conclusion may be true for certain viscous oils and water-in-oil emulsions but the scientific literature supports the conclusion that light oils readily and rapidly disperse.

It has been known for many years that it is more difficult to disperse a high viscosity oil than an oil of low or medium viscosity. Some laboratory testing has shown that the effectiveness of dispersants may be related to oil viscosity, being most effective when the oil viscosity is about 1,000 or 2,000 mPa.s and then declining to a lower level of effectiveness as the oil viscosity approaches 10,000 mPa.s. It was therefore considered that some generally applicable viscosity limit, such as 2,000 or 5,000 mPa.s could be applied to all oils. However, recent work has shown that this is not necessarily the case and modern oil spill dispersants are generally effective up to an oil viscosity of 5,000 mPa.s or more. Some research has shown that their performance does gradually decrease with increasing oil viscosity and that oil with a viscosity of more than 10,000 – 20,000 mPa.s may not be effectively dispersed (see Figure 5).[18]

Figure 5 – Wave Basin Dispersant Effectiveness vs. Oil Viscosity



The data in Figure 5 indicate that oil viscosity alone does not control dispersant effectiveness. Oil composition appears to be as important as viscosity and that these are only two of several factors that affect dispersant performance. Other important factors include the amount of energy being transmitted to the slick from waves, the degree of oil weathering (i.e., the extent to which lighter hydrocarbon components have evaporated), emulsification (i.e., the extent to which water has been entrained in the continuous oil phase), the dispersant type and the dispersant treatment rate (also known as the dispersant-to-oil ratio, or DOR).[19]

Additionally, recent work has shown that dispersant may be applied to oil in ice-infested water using a novel vessel-based maneuverable spray arm system followed by artificial turbulence from propeller wash / jet water to increase mixing energy.[20] This may serve to

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[*] API Gravity is defined as: 141.5/SG – 131.5, where SG is the specific gravity of the fluid being evaluated. In the case of water, SG = 1.0 and API Gravity = 10. The lower the SG, the higher the resulting API Gravity

enhance response effectiveness as oil viscosity increases, as well as showing good potential for smaller spills in ice in general.

Dispersant to Oil Ratio Discussion

Surface vs. Sub-Sea Dispersant Use

Over 4,000 m^3 (25,000 bbls, 1 million gallons) of dispersant were applied to the surface waters of the Gulf of Mexico during the Deepwater Horizon incident.[21] The standard application ratio to achieve effective dispersion, as a baseline application, has been defined as 1 part dispersant to 20 parts oil for surface application (a DOR of 1:20), although the Macondo oil released during the Deepwater Horizon incident has readily dispersed at a DOR as low as 1:250. [22,23]

Figure 6 - Aerial Dispersant Application

Image from Oilspillcommission.gov[24]

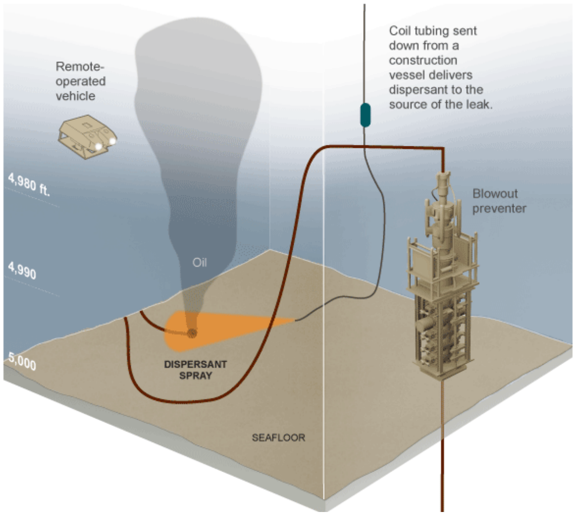
Almost 3,000 m3 (over 18,000 barrels or 700,000 gallons) of dispersant were applied via sub-sea injection directly at the wellhead during the Deepwater Horizon incident.[17]

Considering the oil was very low in viscosity, fresh, concentrated, and discharging into very turbulent conditions, application of dispersants at the wellhead was likely highly efficient, perhaps approaching the effective dispersion ratio of 1 part dispersant to 250 parts oil found for the Macondo oil as discussed above.

As opposed to the primarily aerial application of the surface use of dispersants, the sub-sea introduction of dispersants allowed for the possibility of treating the concentrated release on the sea floor in an extremely effective manner. As the schematic diagram shows in Figure 7 (a), the dispersant was fed into the oil release by means of coiled tubing extended from a surface vessel. Photography of a wand used to deliver the dispersant at an early stage of the spill, Figure 7 (b), indicates that even though it was not always directly inserted into the cloud of oil, it appears that delivery was effective as evidenced by the dispersant moving into the oil.

Figure 7 - Sub-Sea Dispersant Application

(a)



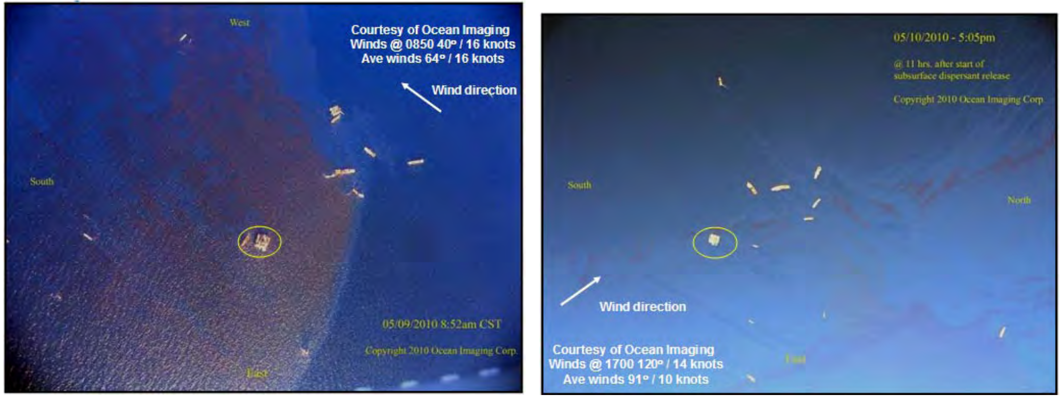
(b)

(a) http://www.oilspillcommission.gov/media/response/response-actions-dispersants.html
(b) Used with permission. © BP p.l.c.

The turbulence associated with the oil and gas plume is quite evident. The volumetric gas-to-oil ratio (GOR) at standard conditions was about 3000:1. At the temperatures and pressures experienced 1,500 meters below the sea surface (4°C and 2,200 psi), the volumetric ratio is closer to 1:1[25].

As is apparent in the following aerial photographs (Figure 8) taken during the DWH incident, the use of sub-sea dispersant delivery may have significantly reduced the surface expression of released oil. Before sub-sea injection, a large surface slick was present. After 11 hours of injection, the surface slick near the well site appears to be much reduced.

Figure 8 – Before (left aerial image) and after 11 Hours of Sub Sea Dispersant Injection (right aerial image).



Images courtesy of Ocean Imaging

Dispersants – the Future State

Following the Deepwater Horizon incident, a number of questions were raised regarding dispersant effectiveness and additional research will provide valuable insight into addressing these questions.

For example, with respect to dispersant effectiveness:

Questions that Remain Unresolved During the DWH Incident

- Do dispersants work effectively in low energy (quiescent sea surface states) mixing regimes?
- Is there a dependable performance measurement extrapolation that may be used to translate from lab and basin studies to the real world?
- Can known characteristics of the oil be used to estimate dispersant effectiveness as the oil weathers and emulsifies?

New Questions that Resulted from the DWH Incident

- Can dispersant effectiveness in high pressure (and low temperature) environments be accurately modeled and the results used to optimize dispersant use?
- Can dispersant effectiveness in high energy, high encounter rate (turbulent sub-sea release) regimes be accurately modeled and the results used to optimize dispersant use?
- Can the interactions of dispersant constituents with oil/gas mixture be modeled and the results used to understand dispersant effectiveness?
- Are there new, more effective formulations that work for a variety of oil spills at much lower DORs (e.g., <1:250)?
- Are there “green” materials or processes that can be used in the production of dispersants?
- How can the general public become educated about dispersants, their use and value as a response tool?

R&D Needed to Resolve Outstanding Questions

The large scale use of dispersants during the Deepwater Horizon incident has helped identify the need for a thorough review of the understanding of this response option. This is especially true with respect to its efficacy in minimizing environmental impacts, identification of the products that may be most effective, the environmental conditions under which dispersants are most effective, and the factors that most influence their performance.[26] Information that results from such a technical review will allow for the identification and description of key areas that will be most amenable to new or continuing research.

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Degradation of Dispersants and Dispersed Oil

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Introduction

Chemical oil dispersants are proprietary mixtures of surfactants and solvents which are directly applied to a spill in order to reduce the natural attractive forces of the oil. When oil treated with dispersants is exposed to mixing energy, typically from wind and wave action, it is broken up into small droplets which may then become entrained in the water column (Li et al., 2009a; Li et al., 2009b; Li, 2008; Lunel, 1995). Many of these droplets are small enough to be neutrally buoyant, and therefore, advection and diffusion forces dilute the plume and transport the droplets far from the site of the original spill. As compared to a surface oil slick or larger and more buoyant physically dispersed oil droplets, these chemically dispersed droplets are much easier for oil-degrading bacteria to colonize and break down (Venosa and Holder, 2007; Venosa and Zhu, 2003). 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 are effectively reduced below toxicity threshold limits, and biodegradation becomes the most important process in reducing the total mass of petroleum hydrocarbons in the environment. By enabling rapid dispersion and biodegradation of surface oil slicks at sea, the use of chemical oil dispersants can be effective in preventing heavy oiling of sensitive coastal environments such as beaches and wetlands, and consequently mitigates risk associated with marine and terrestrial wildlife coming into direct contact with a slick.

Biodegradation of Oil

Any discussion on the biodegradation of chemically-dispersed oil must consider the degradation of the oil itself. A variety of microorganisms in both terrestrial and marine environments have the capacity to utilize petroleum hydrocarbons as the sole source of carbon and energy (Head et al., 2006; Leahy and Colwell, 1990; Atlas, 1981, 1984; ZoBell, 1973). Recently a 181 genera of bacteria, 163 genera of filamentous fungi and yeast, and 22 genera of algae have been identified to have the ability to degrade hydrocarbons by metabolizing them in order to grow (Prince, 2010a,b). These findings are not surprising considering the fact that marine microorganisms have long been exposed to significant quantities of petroleum hydrocarbons from natural seepages.

From 1990 to 1999, approximately 600,000 tons of petroleum were released into the world’s oceans per year from natural seepages (NRC, 2003; Stout and Wang, 2008). Biodegradation by indigenous microbial communities is the major process responsible for the weathering and eventual removal of oil from natural seeps that enters the marine environment (Atlas, 1995; Atlas and Bartha, 1992; Leahy and Colwell, 1990). Within the marine environment, bacteria are the predominant hydrocarbon degraders (Head et al., 2006; Venosa and Zhu, 2003). Studies from tropical to cold Antarctic and Arctic environments have verified their ubiquitous distribution and their ability to multiply rapidly upon the introduction of oil (Atlas, 1995).

Biodegradation rates have been shown to be the highest for saturates, followed by light aromatics, with high-molecular-weight aromatics and polar compounds exhibiting extremely low biodegradation rates (Prince, 2010c). Co-metabolism plays an important role in oil biodegradation and may require microbial consortia or syntrophic interspecies cooperation (McInerney et al., 2008). Many complex branched, cyclic, and aromatic hydrocarbons, which otherwise would not be biodegraded individually, can be oxidized through co-metabolism in an oil mixture due to the abundance of other substrates that can be metabolized easily within the oil (Atlas, 1981).

It is important to note that microorganisms produce extracellular biosurfactants to promote the formation of oil-in-water emulsions that aid in the uptake and subsequent degradation of hydrocarbons (Desai and Banat, 1997). The hydrophilic and hydrophobic components within the biosurfactants emulsify hydrophobic hydrocarbons, and allow for transport into the hydrophilic intracellular space for biodegradation (Southam et al., 2001). In addition, the fatty acid moieties of biosurfactants promote the growth of microorganisms on the surface of oil droplets (Rosenberg et al., 1979). Nikolopoulou and Kalogerakis (2008) reported that the use of rhamnolipid biosurfactants increased removal of weathered petroleum hydrocarbons (96% removal of C19–C34 n-alkanes within a period of 18 days) and reduced the lag phase prior to the onset of biodegradation. Saeki et al. (2009) showed that addition of biosurfactant JE1058BS to seawater stimulated the degradation of weathered Alaska North Slope 521 crude oil by stimulating the activity of the indigenous marine bacteria and facilitating the removal of oil from the surface of contaminated marine sediments.

In terms of the influence of environmental factors controlling natural oil biodegradation rates, field studies have shown that active microorganisms living in low-temperature environments are dominated by two groups: psychrophilic and psychrotolerant, which are sometimes called psychrotrophic (Atlas, 1984). As defined by Morita (1975), psychrophiles experience optimum growth at less than 15°C, with a maximum growth temperature below 20°C and a minimum growth temperature at or below 0°C. Despite living at these low temperatures, psychrophiles often have metabolic rates comparable to those displayed by the mesophiles adapted to more moderate temperatures. For example, Delille et al. (2009) reported that a temperature of 4°C in the Antarctic had little effect on biodegradation efficiency and that the nutrients, nitrogen and phosphorus, were the limiting factors. Results obtained by Siron et al. (1995) indicated that the temperature threshold for observing significant oil biodegradation was around 0°C. Decreases in solubility associated with low temperatures were considered to be a causal factor for the cases of observed recalcitrance of hydrophobic compounds in cold-water. However, recent reports have indicated that some bacteria may have adapted to the low solubility of hydrophobic environmental chemicals (Deppe et al., 2005; Wick et al., 2002). Indeed there is now evidence that hydrocarbon-degrading microbes may have novel uptake mechanisms that enable them to degrade hydrocarbons at rates that exceed their rates of dissolution in the aqueous phase (Leahy and Colwell, 1990; Thomas et al., 1986).

Throughout the world, the salinity of seawater averages about 35‰ (parts per thousand). Salinity variations, albeit small, are mainly caused by such factors as melting of ice, inflow of river water, evaporation, rain, snowfall, wind, wave action, and ocean currents that cause horizontal and vertical mixing of the saltwater (Lagerloef et al., 1995). Most marine species have an optimum salinity range of 25–35‰ (ZoBell, 1973) and species living in the transition environments are well adapted to fluctuations in salinity. Microorganisms requiring salt for growth are referred to as halophiles. Whereas halophilic hydrocarbon-metabolizing bacteria perform well in this salinity range, there have been reports of the isolation of bacteria capable of degrading hydrocarbons above a salinity of 35‰. Bertrand et al. (1990) reported the isolation from a salt marsh of an extremely halophilic archaea bacterium capable of degrading hydrocarbons in 204‰ NaCl, but not below 105‰. Diaz (2008) reported the isolation of a bacterial consortium, which mainly included members of the genera *Marinobacter*, *Erwinia* and *Bacillus*, from a crude oil sample from the Cormorant field in the North Sea. This consortium was able to metabolize petroleum hydrocarbons in a salinity range from 0 to 220‰ NaCl. Total oil degradation ranged from 48% to 75%, with the greater degradation occurring at the lower salinities.

At the sea surface, wind and wave action maintain a constant supply of oxygen, thus aerobic catabolism of hydrocarbons is usually the preferred biochemical pathway (Leahy and Colwell, 1990). Oxygen may become limiting in subsurface sediments and anoxic zones of the water column. Oxygen limitation is also a concern for most fine-grained marine shorelines, freshwater wetlands, mudflats and salt marshes (Venosa et al., 2002a; Venosa and Zhu, 2003). It is commonly believed that biodegradation rates under anaerobic conditions are almost negligible, while aerobic biodegradation of hydrocarbons occurs rapidly. However, the importance of anaerobic biodegradation should not be underestimated as it has been shown to be a major process under certain conditions. In anoxic marine sediments, reductions of sulphate, Mn(IV) and Fe(III) are the primary terminal electron-accepting processes (Canfield et al., 2005; Finke et al., 2007). Hydrocarbon degradation coupled with sulphate reduction prevails in marine anoxic sediments (Lovley et al., 1997).

With recent advances in analytical methods such as genomics, we are now able to determine the potential of whole microbial communities for oil biodegradation at low temperatures. New evidence as a result of advances in the field of environmental genomics suggests that crude oils are degraded by indigenous organisms in cold water environments at a higher rate than previously reported. This is not surprising since natural oil seeps occur in the world's oceans at great depths and low temperatures – microbes have become well adapted to their surrounding environment. Studies have conclusively shown that elevated concentrations of hydrocarbons in the environment increase the number of catabolic-gene copies among the microbial community (Heiss-Blanquet et al., 2005; Stapleton and Sayler, 2000; Whyte et al., 2002).

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 (National Research Council, 2005). Whereas some studies observed stimulation of biodegradation rates by the use of chemical dispersants (Swannell and Daniel, 1999; Traxler and Bhattacharya, 1978), chemical dispersion inhibited the biodegradation rate or had no effect in other studies (Foght and Westlake, 1982; Lindstrom and Braddock, 2002). 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 (Foght et al., 1987; Van Hamme and Ward, 1999). 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) (Foght et al., 1987; Lindstrom and Braddock, 2002). 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 (Van Hamme and Ward, 1999; Varadaraj et al., 1995).

Attempts have been made to predict the rate of oil biodegradation in the environment based on the results of laboratory studies using scalable, quantitative biodegradation kinetics models that treat oil as droplets suspended in water rather than as homogenous solutions of hydrocarbons in water and consider the growth of the organisms responsible for the biodegradation of oil (National Research Council, 2005). To date only two studies have made an attempt to estimate biodegradation kinetic parameters (Venosa and Holder, 2007; Zahed et al., 2011), by measurement of first-order (in oil concentration or the concentrations of specific oil components) rate coefficients to enable comparison among treatments. However as only one independent rate coefficient was estimated for each treatment, treatment effects could not be rigorously evaluated.

Conducting representative biodegradation studies on dispersed oil in microcosm-scale test systems has at least two important challenges that researchers need to consider as they develop test protocols (Lee et al., 2011). One challenge is to conduct tests at the low dispersed oil concentrations representative of field conditions. Many previous biodegradation studies were conducted at unrealistically high concentrations of dispersed oil in closed microcosms. Prior research either failed to recognize the rapid dilution that occurs at sea or employed methods that were not sufficiently sensitive to study low concentrations. Studying dispersed oil biodegradation at concentrations several orders of magnitude above expected at-sea concentrations in closed systems could limit biodegradation rates and total degradation by exhausting the available nutrients. Some researchers attempted to address this by adding nutrients to the system, but this can lead to unrepresentative modification of the microbial community.

The second challenge with studying dispersed oil biodegradation in a closed system is the difficulty of maintaining a stable dispersion in the laboratory. Dispersed oil in the water column exists as small droplets that neither surface nor sink, and the droplets become so scattered that they cannot coalesce. It is challenging to maintain stable dispersions of oil in closed systems during the often multi-week test periods required to conduct biodegradation studies. To simulate the dispersion of oil at sea, biodegradation studies require formation of a stable dispersion containing droplets no greater than 70 - 100 microns and enough mixing energy to keep droplets from resurfacing during an experiment.

A recent Joint Industry Program (McFarlin et al., 2011) on the biodegradation of oil under Arctic conditions has assessed biodegradation of chemically and physically dispersed Alaska North Slope oil as indicated by both primary degradation and hydrocarbon mineralization. The study was conducted under low ambient temperature conditions (-1oC – 2oC) and relatively low oil concentrations (10-12 ppm crude oil in seawater) and under low level nutrients (0.5 – 1% of the OECD recommended volume of Bushnell Haas Broth). The results of the study demonstrated that the use of dispersant increased the primary biodegradation of fresh oil from 37% to 56% and the mineralization from 12% to 27%. Further increment was due to the addition of nutrients by 10 % for both primary degradation and mineralization.

Biodegradation of Dispersants

Most studies on surfactant biodegradation focus on surfactants that are used in high-volume consumer products, such as laundry detergents (e.g., linear alkyl sulfonates), or other cleaning agents which have known environmental health and safety concerns (e.g., alkylphenol ethoxylates). In general, the results of these have shown that most surfactant formulations are fairly readily biodegraded under aerobic (oxygen present) conditions by marine bacteria (Lee et al., 1985; Liu, 1983; Una and Garcia, 1983). The rate of biodegradation under anaerobic (absence of oxygen) conditions tends to be much lower (Berna et al., 2007; Ying, 2006). Research into the anaerobic biodegradability of sulphonate-based (anionic) surfactants has shown that chemical composition and molecular orientation can play an important role in biodegradability of a particular compound. Through the use of anaerobic digesters and analyses of bacterial biogas production, Garcia et al. (2009) conducted a series of batch degradation experiments which revealed that the anaerobic biodegradability of branched alkyl sulphosuccinates such as those used in Corexit were much lower (≤50% mineralization after 50 days) than that of linear alkyl sulphosuccinates (≥ 80% mineralization after 50 days). It is clear that different types of surfactants, and even individual surfactants of the same class, can biodegrade at very different rates depending on the structural complexity of chemical branching.

A report by the Fraunhofer Institute (2003) discusses in detail the anaerobic biodegradation of detergent surfactants such as those used in household cleaners. Unfortunately, little attention is paid to the surfactants commonly found in chemical oil dispersants. Generally speaking, the report states that non-ionic surfactants are readily biodegradable under both aerobic and anaerobic conditions. While anionic surfactants based on sulphosuccinate are readily biodegraded under aerobic conditions, data is limited concerning their anaerobic biodegradability.

The biodegradation of surfactants used oil spill treatment agents has been studied for years (Baumann et al., 1999; García et al., 2009; Lindstrom and Braddock, 2002; Liu, 1983; Odokuma and Okpokwasili, 1992; Una and Garcia, 1983). Surfactant biodegradation studies usually distinguish between primary biodegradation, which was calculated from the overall mass balance of surfactant in the reactors (García et al., 2009; Una and Garcia, 1983), and ultimate biodegradation, which also considers the removal of the intermediate products, usually based on oxygen consumption (Odokuma and Okpokwasili, 1992) or carbon dioxide production (García et al., 2009; Lindstrom and Braddock, 2002) relative to the amount expected based on the compound structure. Extensive, but incomplete, primary biodegradation of the ethoxylated non-ionic 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 (Una and Garcia, 1983). Primary biodegradation of Span 80, the unethoxylated non-ionic 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 (Baumann et al., 1999), and DOSS (dioctyl sodium sulfosuccinate) was extensively biodegraded by activated sludge bacteria (García et al., 2009), but the observed oxygen consumption or carbon dioxide production were much lower than expected for Corexit 9527 (Odokuma and Okpokwasili, 1992) and Corexit 9500 (Foght et al., 1987), respectively, suggesting that biodegradation was incomplete within the testing period. 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 (Baumann et al., 1999; Kim and Weber Jr., 2003). Note, however, that enzymatic oxidation and subsequent metabolism of polyethoxylate groups has been described (Nguyen and Sigoillot, 1997; Owen et al., 1997).

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, the methods used to monitor biodegradability (as the separation of surfactants and the crude oil hydrocarbons remains a challenge in analytical chemistry), and hence again the critical importance of testing biodegradability at environmentally relevant substrate concentrations. Unfortunately, until the recent Deepwater Horizon oil spill in the Gulf of Mexico, little information is available on the fate of surfactants in the presence of natural microbial seawater communities at concentrations expected during actual spill response operations. .

Toxicity and Bioaccumulation of Dispersant Surfactants

The toxicity of dispersants may influence trophic level dynamics including microbial processes responsible for oil degradation (Lee et al,, 1985). The premise of dispersant use is based on the reduction of oil to concentrations below toxicity threshold limits. Based on the results of toxicity tests for EPA-approved dispersants such as Corexit 9527 and 9500 listed on the National Contingency Plan (NCP) Product Schedule and the recommended dispersant-to-oil (DOR) application rates, major environment impacts were not expected at the concentrations to be encountered during their operational use for the treatment of oil spills. A report from the Centers for Disease Control and Prevention (2010) also 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."

Despite the development of a regulatory approval mechanism for the support of their operational use, a considerable amount of ongoing research has been funded to evaluate the toxicity of chemical oil dispersants in the marine environment. Public concerns remain high in regards to this topic as the data collected to date has been highly variable due to factors such as differential sensitivity between species, the particular dispersant formulation used, and experimental conditions used (George-Ares and Clark, 2000; Lyons et al., 2011).

Ramachandran et al. (2004) reported that cchemically-dispersing different crude oils increased the exposure of fish to the constituents of oil by 10 to 1000-fold in comparison to undispersed oil. The enhanced exposure was demonstrated by an increased activity of liver enzymes that oxygenate compounds accumulated from water containing chemically-dispersed oil droplets. The implication of this work is that the toxicity of oil to fish increased following chemical dispersion in proportion to the extent to which the oil was dispersed. It was noted that the amount of a solution of chemically-dispersed oil that caused toxicity was 100 times less than the amount of undispersed oil required to cause the same effect. However, the measured concentrations of hydrocarbons that were toxic was virtually the same between solutions of dispersed and undispersed oil. Thus, the effect of chemical dispersion was to transfer more compounds from oil to water, and not to make these compounds more toxic.

A study conducted by Fuller et al. (2004) using two fish species, *Cyprinodon variegatus* and *Menidia beryllina*, one shrimp species, *Americamysis bahia* (formerly *Mysidopsis bahia*), and the luminescent bacteria *Vibrio fisherithese* indicated that the toxicity of chemically dispersed oil preparations was equal or less toxic than that of the oil alone. A separate study by Hemmer et al. (2010) looking at toxicity of Louisiana Sweet Crude (LSC), chemical oil dispersants, and chemically dispersed LSC on *M. beryllina*, and *A. bahia* reported that the toxicity of the dispersant alone was lower than that of LSC or dispersed LSC which both showed moderate to high toxicity. Similarly, Milinkovitch et al. (2011) found that while containment and recovery of spilled oil is optimal, there is no significant difference between the toxicity of naturally and chemically dispersed oil when looking at a series of biomarker responses in the gills of golden grey mullet (*Liza aurata*). Further work by Judson et al. (2010) has investigated the potential for chemical oil dispersants to interfere with hormone and other bio-chemical processes in marine organisms. The results of this study concluded that while some dispersants did show low potential for endocrine disruption, most (including Corexit) did not show any significant effect.

Brief pulses of chemically-dispersed oil can be just as toxic to fish embryos as prolonged exposures. McIntosh et al. (2010) recently reported that exposures to chemically-dispersed crude oil as brief as one hour prevented the fertilization of Atlantic herring embryos. Similarly, one-hour exposures immediately following egg fertilization were sufficient to cause deformities, interfere with development, and kill herring embryos at oil concentrations typical of those measured near actual marine oil spills. Thus, contrary to expectations, the primary concern about oil dispersion may not be the toxicity of chemical dispersants, nor the enhanced toxicity of oil. Rather, it is the greatly increased exposure of highly sensitive embryos to the toxic components of oil. As the result, there is the possibility that even brief exposures of fish embryos to dispersed oil can cause embryo toxicity at oil concentrations typical of actual spills. The results of these laboratory studies have highlighted the need for future research to determine effects under the environmental conditions encountered under operational response operations.

In light of the toxicity research study results obtained for chemical oil dispersants, it is suggested that factors such as toxicity of dispersed oil (rather than dispersant itself), dilution and degradation in the environment, species/resources requiring priority protection, potential adverse effects of all response options, and the potential for recovery of sensitive habitats and populations should weigh more heavily into the decision making process than dispersant toxicity alone George-Ares and Clark (2000). Supporting this view, a recent review of the use of chemical dispersants in Europe found that ongoing improvement in dispersant formulation has now reached a point where the toxicity of the dispersant itself is much less important than the toxicity of the oil it is dispersing (Chapman et al., 2007).

While the focus of studies on chemically dispersed oil has been on the induction of acute and/or chronic toxic effects for risk assessments associated with dispersant use, some consideration has also been given to the bioaccumulation of surfactants. In a study on the uptake of two linear alkylbenzene sulfonates by a freshwater oligocheate (*Lumbriculus variegatus*) and a larval insect (*Chronomus riparius*) using radioactive tracers Mäenpää and Kukkonen (2006) reported that the surfactant residue in the body of the test organisms was more highly dependent on the organic content of the test sediment than on the initial exposure concentration. It was concluded that the high organic content of the test sediment reduced body residue concentrations due to the 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 but that environmental variables could reduce the concentration of surfactants associated with the test species (EOSCA, 2000).

Following a comprehensive review on the bioaccumulation potential of surfactants, the European Oilfield Specialty Chemicals Association (EOSCA) concluded 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 (EOSCA, 2000). There is also evidence that non-ionic and anionic surfactants (such as those found in most oil dispersants) are biotransformed and eliminated via the gall bladder (Tolls et al., 1994) As a result of surfactant metabolism, Comber et al. (2003)

suggested that linear alkylbenzene sulfonates, alcohol ethoxylates, and other structurally similar surfactants are unlikely to bioaccumulate to any significant degree.

Dispersant Use During the DWH Spill Response

The decision by the EPA, NOAA and BP to use chemical dispersants at the Deepwater Horizon spill site did not come lightly. The United States Clean Water Act specifically addresses the use of dispersants in response to oil spills in Section 311(d)(2)(G) which requires that the federal National Contingency Plan for oil spill response contain a schedule identifying:

> (i) dispersants, other chemicals, and other spill mitigating devices and substances, if any, that may be used in carrying out the Plan,
>
> (ii) the waters in which such dispersants, other chemicals, and other spill mitigating devices and substances may be used, and
>
> (iii) the quantities of such dispersant, other chemicals, or other spill mitigating device or substance which can be used safely in such waters, which schedule shall provide in the case of any dispersant, chemical, spill mitigating device or substance, or waters not specifically identified in such schedule that the President, or his delegate, may, on a case-by-case basis, identify the dispersants, other chemicals, and other spill mitigating devices and substances which may be used, the waters in which they may be used, and the quantities which can be used safely in such waters.

Although Corexit 9527 and 9500 were both pre-approved by the EPA for use in the event of an oil spill, until the incident in the Gulf, little consideration was given to the suitability of these products for subsurface application. Subsurface injection of dispersant was considered as a means to reduce VOC levels and the volume of dispersant to be used (as application at the well head would improve contact between dispersant and the oil). Thus, regulatory approval subsurface application was withheld until its efficacy and potential effect on the environment could be assessed (EPA Press Conference Call, 2010).

Following a Net Benefit Environmental Analysis (NEBA) process, a decision was made to apply dispersions an operational countermeasure during the Deepwater Horizon response operations. In Total, 43,884 barrels of Corexit brand chemical oil dispersant was applied (1); 25,505 barrels of Corexit 9527 and Corexit 9500A at the surface (by spraying from vessels at sea and aircraft) and 18,379 barrels of Corexit 9500 via subsurface injection (Federal Interagency Solutions Group, 2010).

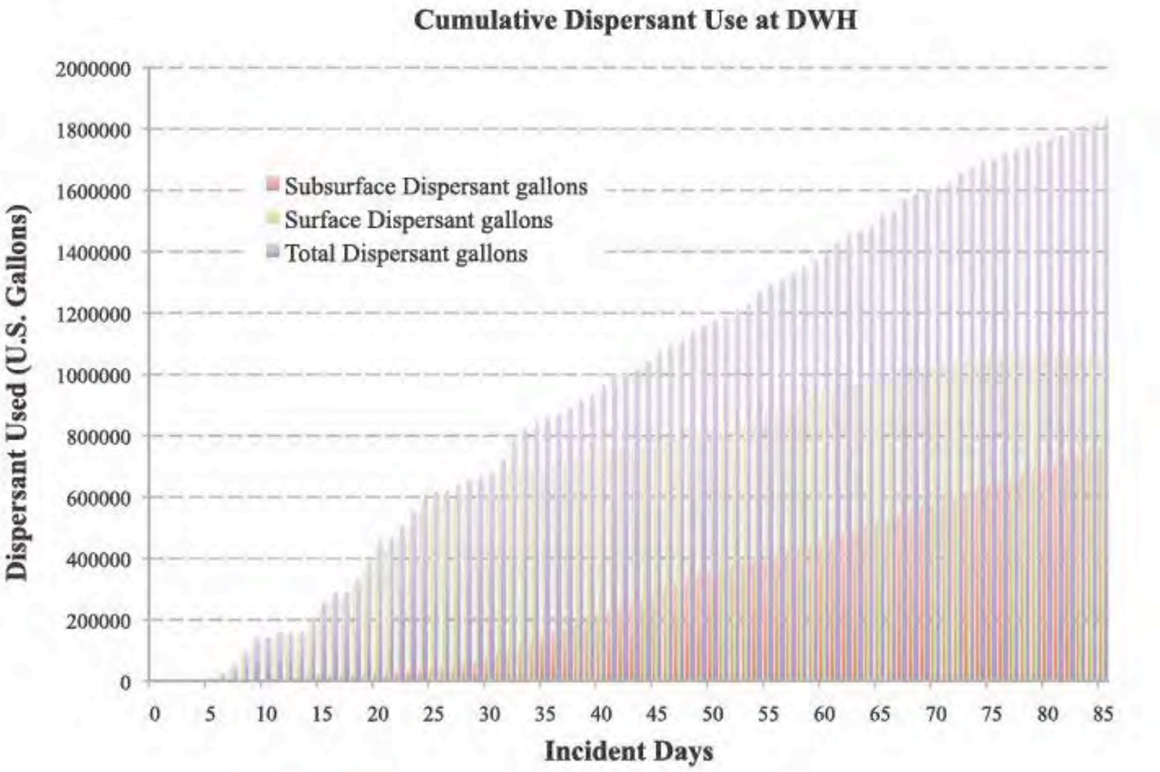

Figure 1. Cumulative surface and subsurface dispersant use by day of spill response (Federal Interagency Solutions Group, 2010).

Dispersant Transport and Fate following the DWH Spill

Corexit 9500 and 9527 were the main dispersants used in response to the BP-*Deepwater Horizon* oil spill. Detailed formulation and ingredient information on COREXIT dispersant products were released to the US EPA for its Gulf monitoring and environmental risk assessment program (Nalco, 2011). The surfactants in these products are similar, including several non-ionic compounds-sorbitan monooleate (Span 80), polyethoxylated sorbitan monooleate (Tween 80), and polyethoxylated sorbitan trioleate (Tween 85)—and the anionic surfactant diethylhexyl sulfosuccinate (DOSS) (Nalco, 2011), but the relative proportions of these compounds may differ somewhat between products (Kujawinski et al., 2011). The biodegradability of chemical constituents was a criterion in the selection of their formulation by the manufacturer to minimize potential for risks to the environment or public health associated with its use.

As the dispersants could be broken down rapidly in seawater; the individual chemical constituents 2-butoxyethanol, dipropylene glycol n-butyl ether (DPnB), propylene glycol, and dioctyl sodium sulfosuccinate (DOSS) were selected for analysis of water samples to determine the expanse of the Deepwater Horizon dispersed oil and Corexit (Operational Science Advisory Team, 2010). These compounds represent major constituents of Corexit, including those with known toxicology data, and also those with newly established analytical methods.

Benchmark levels for the individual compounds are established to explain the relevance of measured concentrations (i.e., concentrations above benchmark levels are "levels of concern.") The benchmarks were based on available biological effects data were set at a conservative level to protect aquatic life. It was also recognized that the target compounds were also used in other commercial products besides Corexit. Thus, the other sources of the individual chemicals were to be considered if the benchmark values were exceeded.

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 one of the most commonly observed dispersant indicator compounds (57 of the 60 positive water samples), but its concentration never exceeded 3 µg/L (Table 1).

Table 1. Samples from the Gulf of Mexico analyzed for the presence of Corexit dispersant indicators; data from the Operational Science Advisory Team (2010).

Zone	Profile	Undetected	Below Benchmark
Nearshore	water column	4790	60
	Sediment	406	6
Offshore	water column	251	199
	Sediment	242	1
Deep Water	water column	3761	353
	Sediment	119	1

* no exceedence of EPA's dispersant benchmarks were observed.

Propylene glycol was the only dispersant indicator detected in the nearshore sediments. Concentrations of DPnB decreased over time (Figure 2), with all values less than 5 µg/L by July 30. The DPnB concentration was highest at the surface and subsurface between 1000 and 1400 m (Figure 3). Deep water concentrations ranged from 0.0170 to 113.4 ìg/L with a mean of 4.3 ìg/L (Operational Science Advisory Team, 2010).

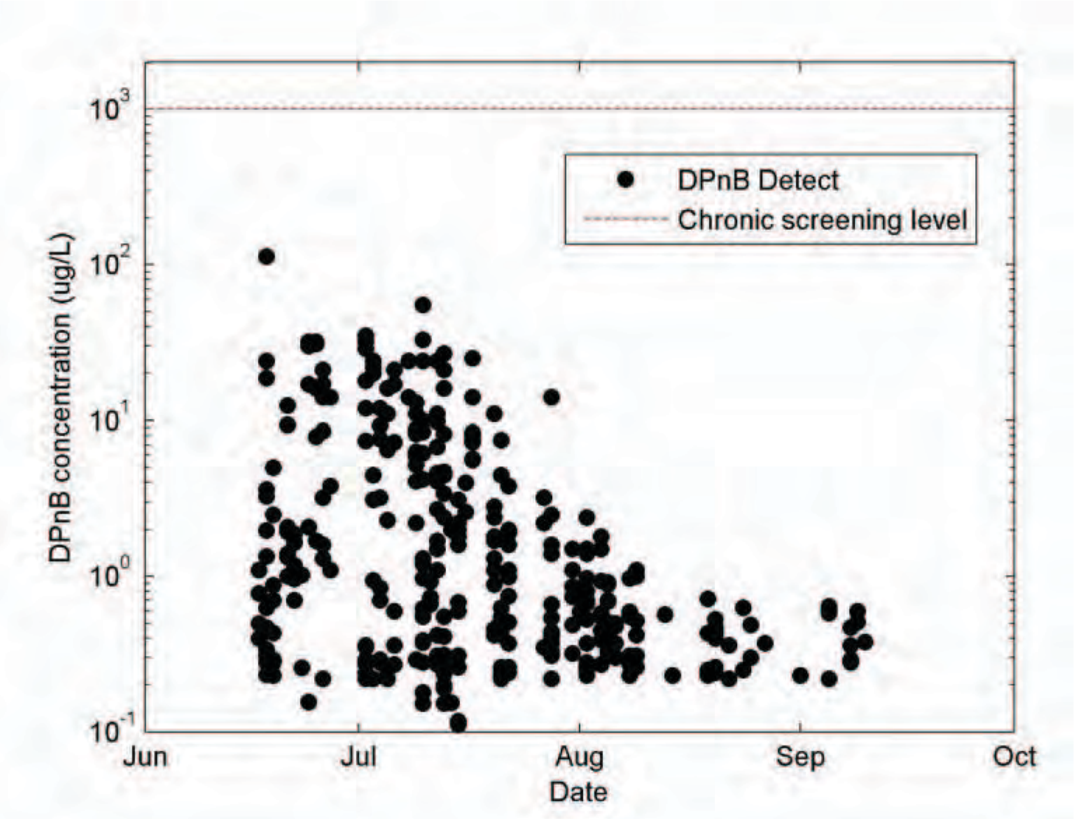

Figure 2. Offshore DPnB concentration over time; the United States Environmental Protection Agency benchmark (chronic screening level) is 1 mg/L (Operational Science Advisory Team, 2010).

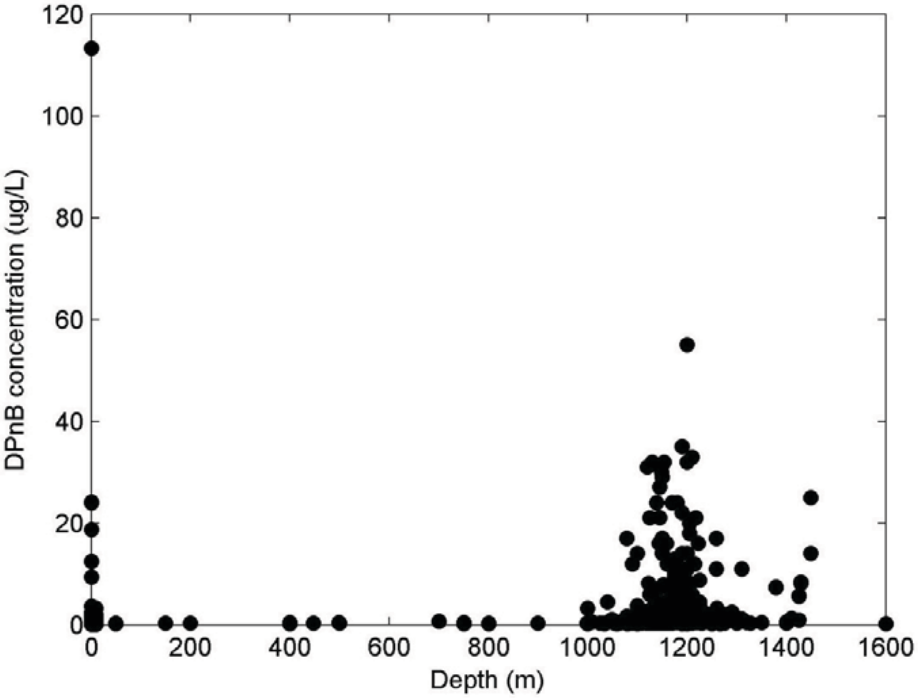

Figure 3. Concentration of DPnB with depth in water samples collected in the deep water zone of the Gulf of Mexico, defined as water depths of greater than 200 m (Operational Science Advisory Team, 2010).

Using advanced liquid chromatography Fournier transform ion cyclotron resonance mass spectrometry, DOSS was detected both during dispersant application, and up to 300 km from the wellhead 64 days after deepwater dispersant injection had ceased (Kujawinski et al., 2011). It was reported that the majority of the DOSS associated with the subsurface injection of Corexit 9500 moved to, and remained in the bottom water layer between 1000 and 1200 m depth rather than rising to the surface (Figure 4). The possibility could not be dismissed that some dissolution with subsequent vertical transport, as well as partitioning with gas or hydrate, might have occurred. The near 1:1 correlation between DOSS and methane (which was found to act as a conservative marker in this situation) and the consistency between their release rates, indicated that DOSS was not biodegraded or otherwise lost near the well head during conditions of active flow, and thus was transported to the 1000-1200 m layer (Figure 5). The measured concentrations, ranging from 0.4 to 12 µg/L, were remarkably similar to the expected estimated concentrations. Based on the data, Kujawinski et al. (2011) concluded that although biodegradation might have occurred, the most significant factor that caused a decrease in DOSS concentration at depth was dilution. They calculated that biodegradation rates would have had to be approximately ten times the dilution rate in order for it to have been observed (Kujawinski et al., 2011).

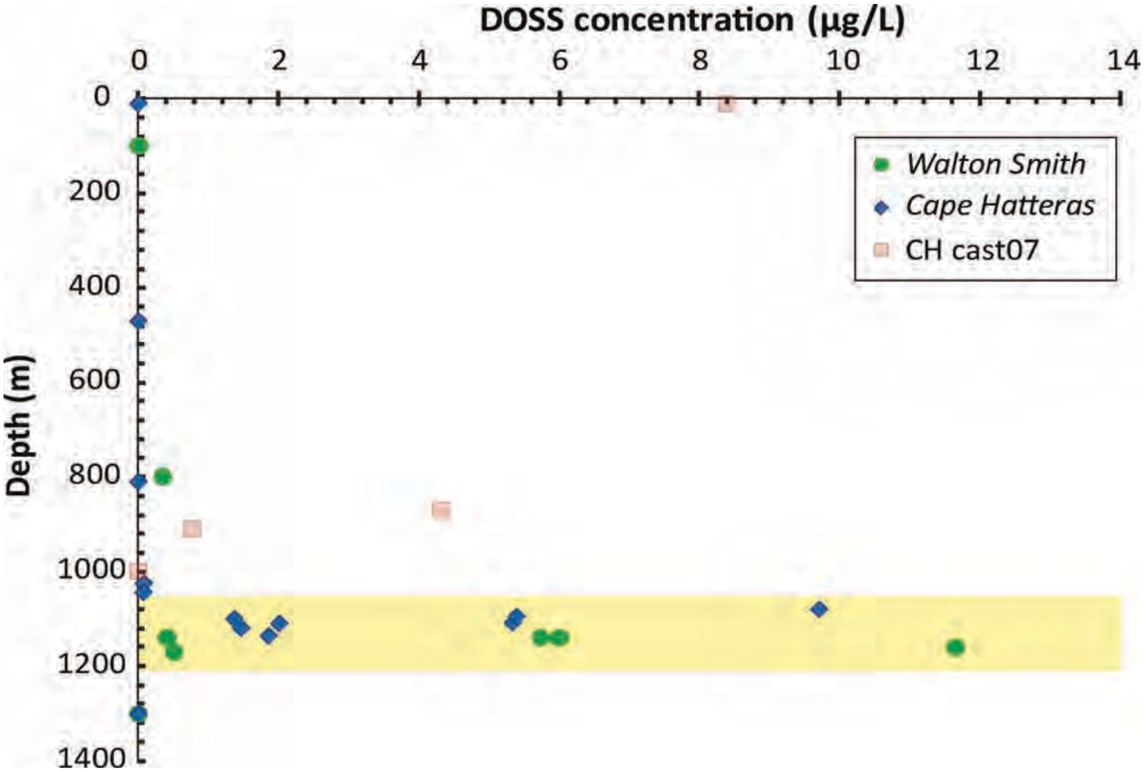

Figure 4. Depth profile of DOSS concentrations falling mainly in the high chromophoric dissolved organic matter zone which included high levels of methane (yellow area), during May and June,

2010, from samples collected by the research vessels *Cape Hatteras* (CH) and *Walton Smith*, with anomalous values from cast07 (Kujawinski et al., 2011).

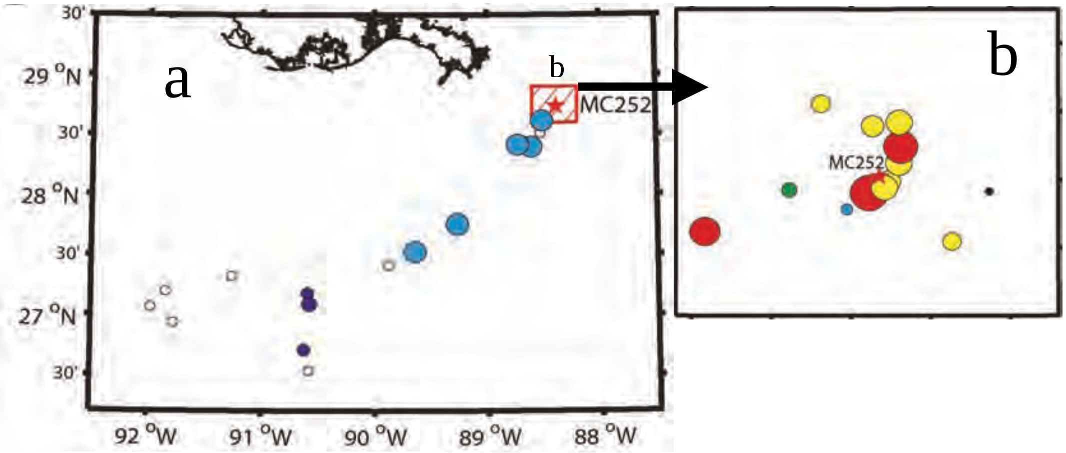

Figure 5. Bird's-eye view of DOSS concentrations at the plume depth of 1000-1200 m in September (a) and May/June (b) with circle size and colour indicative of concentration: white is below detection; blue < 0.01 µg/L; cyan 0.011-0.1 µg/L; green 0.11-1.0 µg/L; yellow 1.0-9.0 µg/L; red > 9.1 µg/L; black indicates the samples were not taken in the plume layer; the star indicates the Deepwater Horizon oil spill site (Kujawinski et al., 2011).

Oil Degradation following the DWH Spill

The recent *DWH* spill has highlighted the importance of natural oil degradation in the recovery of marine ecosystems impacted by crude oil spills. Hazen et al. (2010) reported that the disappearance of residual oil in the Gulf of Mexico from the *DWH* spill was associated microbial degradation processes based on the results of metagenomics. Temperature did not appear to be a major limiting factor as significant rates of oil degradation were observed within the subsea plume of dispersed oil at a depth of 1300 m and temperature below 4^{o}C. Unlike oil spills occurring at the sea surface, during the *DWH* spill, petroleum hydrocarbons experienced a prolonged, buoyancy-driven ascent through the 1500 m water column (Hazen et al., 2010). Consequently a unique set of processes affected the released hydrocarbons during their trajectory in the deep sea. Some oil and gas never reached the sea surface, but instead formed hydrocarbon-rich plumes within the cold waters present at about 1100 m depth, supporting an active deep-sea microbial community (Hazen et al., 2010; Valentine et al., 2010). A combination of integrated chemical, physical and biological processes regulated the transport and fate of hydrocarbons in the deep marine environment. Considering the natural levels of variability and the availability of data at this point of time, it is difficult to disentangle the role of natural processes from the effects of countermeasures such as the use of dispersants.

A considerable amount of research has been focused on the resultant plume of dispersed oil and gas released from the well blow-out that extended southwest from the wellhead between about 1000 and 1200 m below the surface (Camilli et al., 2010; Diercks et al., 2010; Hazen et al., 2010; Kessler et al., 2011; Valentine et al., 2010). This plume was identified based on fluorescence (Camilli et al., 2010; Diercks et al., 2010; Hazen et al., 2010), light scattering (Diercks et al., 2010), or the concentrations of specific hydrocarbons (Camilli et al., 2010; Diercks et al., 2010; Kessler et al., 2011; Valentine et al., 2010) and was detectable up to 35 km from the MC252 wellhead (Camilli et al., 2010). The average temperature in the plume was about 5 °C (Camilli et al., 2010; Hazen et al., 2010). 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 (Camilli et al., 2010). Other studies, however, showed good agreement between data from the *in-situ* DO probe and Winkler titrations (Kessler et al., 2011; Valentine et al., 2010), 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) (Kessler et al., 2011; Valentine et al., 2010) and higher molecular weight normal alkanes (Kessler et al., 2011) was obtained based on compositional changes that reflected preferential utilization of specific compounds and (for ethane and propane) changes in °C (Valentine et al., 2010). 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 (Valentine et al., 2010). 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 (Comber et al., 2003). 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 (Hazen et al., 2010). The abundance of genes involved in hydrocarbon degradation were significantly enhanced ($p < 0.05$ or 0.01) in plume samples, and there was a positive correlation with the concentration of low molecular weight components in the oil, suggesting that the composition of the bacterial community changed in response to the presence of oil (Hazen et al., 2010). Cloning and sequencing of 16S rRNA genes showed that the relative abundance of 16 taxa of ã-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 *Oceanospirillales* (Hazen et al., 2010). 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 *Oceanospirillaceae*, 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 (Valentine et al., 2010).

Recently, Lu et al. (2011) showed that the microbial community functional composition and structure were dramatically altered in the deep-sea from the Deepwater Horizon spill.

A variety of metabolic genes involved in aerobic and anaerobic hydrocarbon degradation were highly enriched in the plume than outside the plume. Various other microbial functional genes that are associated with carbon, nitrogen, phosphorous, sulfur, and iron cycling, metal resistance, and bacteriophage replication were also enriched in the plume. The authors suggest that the indigenous marine microbial communities could have a significant role in biodegradation of oil spills in deepwater.

In summary, the size and composition of the Gulf of Mexico microbial community was altered as microbes responded to the presence of oil. Bacterial cell densities were significantly higher in the plume, 10^5 cells mL^{-1}, as compared to numbers outside the plume, which was 10^3 cells mL^{-1} (Atlas and Hazen, 2011). As the community responded, hydrocarbon degraders dominated, resulting in reduced community diversity. DNA surveys for bacterial 16S rRNA genes from samples collected in June revealed dominance of *Cycloclasticus* and *Colwellia*, likely degrading propane and ethane preferentially (Kessler et al., 2011; Valentine et al., 2010). Sixteen taxa of the **γ-**proteobacteria dominated by the order *Oceanospirillales* occurred in high numbers and dominated the community in plume samples collected in the same time frame (Hazen et al., 2010). Among these were *Oliespira antarctica, Thalassolituus oleivorans,* and *Oliphilus messinensis*, bacteria known to degrade hydrocarbons and tolerate low temperatures that occur in the deep sea. Samples collected later (September) indicated a shift away from these hydrocarbon degraders to methanotrophs, including *Methylococcaceae*, *Methylophaga*, and *Methylophilaceae*. The enhanced abundance of methanotrophs and bacteria containing the particulate methane monooxygenase gene (pmoA) indicated that methane was consumed later in the spill sequence by a different bacterial assemblage (Kessler et al., 2010).

Propane and ethane were degraded relatively rapidly and likely before alkanes >5 carbons in length (Valentine et al., 2010). The occurrence of natural seeps in the area of the spill may have supported the development and persistence of microbial communities capable of degrading hydrocarbons. Dissolved propane and ethane may promote rapid hydrocarbon degradation and low diversity communities that can degrade other hydrocarbons as the nature of remaining hydrocarbons changes. Hazen et al. (2010) estimated biodegradation rates for hydrocarbons in the plume based on observed concentrations of C13-C26 alkanes from samples collected near the MC252 plume and from laboratory degradation studies at 5 °C. Based on these observations, degradation of alkanes was estimated to be 1.2–6.1 days. Rapid rates of biodegradation may be expected for alkanes, the least recalcitrant fraction among the complex mixture of compounds that makes up Sweet Louisiana Crude oil. Rapid degradation rates reported for Sweet Louisiana Crude in the region of the MC252 oil spill may be related to its relatively light character, containing a large volatile component and a large fraction of alkanes, both more amenable to degradation than heavier crude oil. Edwards et al. (2011) reported that microbes within the surface slick showed higher rates alkaline phosphate activity, indicating enhanced phosphate stress. Microbial respiration and lipase activity rates were also higher with the slick and the degradation of hydrocarbons was fairly rapid and supported the majority of respiration. The authors suggest that the microbial community possessed the potential to respire hydrocarbons at an unprecedented rate, potentially great enough to keep pace with the flux of oil reaching the surface from the Macondo well, and the observed differences in microbial respiration and activity between stations within the slick and outside the slick is a testament to the rapid response of the microbes in surface waters of the Gulf of Mexico to oil from the Deepwater Horizon spill.

The composition of the oil fraction from MC252 estimated by Reddy et al. (2011) indicated 74% saturated hydrocarbons, 16% aromatic hydrocarbons and 10% polar hydrocarbons. Gas chromatographic analysis for several monoaromatic compounds indicated benzene, toluene, ethylbenzene and total xylenes (BTEX) concentrations exceeding 50 μg L^{-1} within the plume in June 2010 (Camilli et al., 2010). Estimates for hydrocarbon degradation in the plume range from 2–7 μg $L^{-1}d^{-1}$, which translates to an estimated half-life of about 1 month for petroleum hydrocarbons (Reddy et al., 2011). Methane was estimated to take longer to degrade. Kessler et al. (2011) estimated the oxidative lifetime of methane resulting from the spill to be 120 days.

Lessons Learned from Deepwater Horizon Spill Response and Future Challenges

About 2.1 million gallons of dispersant were used during the *Deepwater Horizon* spill response, and about 8% of the oil that was released is thought to have been chemically dispersed (Lubchenco et al., 2010). Based on current knowledge, it is believed that most of the chemically dispersed oil, including the MC252-derived hydrocarbons in the deep plume, may have been biodegraded within the environment following its release. 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. In light of the large uncertainties associated with measurements of hydrocarbon fate following accidental spills, fate and transport modeling may offer the best means for evaluating the relative impacts and benefits of chemical dispersion in spill response.

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, it is impossible to extract concrete evidence to support the hypothesis that the dispersant surfactants biodegraded rapidly in subsurface waters. Additional research is warranted to enhance better and more quantitative understanding of the fate of dispersants and chemically dispersed oil, particularly in subsurface. In terms of potential 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 (Varadaraj et al., 1995).

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Physical Transport and Chemical Behavior of Dispersed Oil

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1. Overview of dispersant transport and chemical behavior of dispersed oil

1.1 Overview of topic as it related to dispersant use during DWH

During response operations, scientific information is provided to decision makers, such as the Federal On-Scene Coordinator (FOSC), state and federal trustees, and the public. The decision to use chemical dispersants during a response is made among all these parties, and during the Deepwater Horizon (DWH) oil spill the dispersant discussion included both surface and subsurface application of chemical dispersants. This paper is intended to provide perspective on research needs considered pre- and post-DWH oil spill related to response modeling and data collection needs for decision support of dispersant application and its potential effects. Given time constraints for implementing models and sampling strategies for response, requirements for data and types of questions to be addressed may be significantly different than requirements for research or damage assessment activities. At the time of this writing, just over a year after the successful response operations to cap the well, many studies are still in progress, and data are still being collected and evaluated to assess dispersant effectiveness and possible impacts. More information and research results will become available over the next months to years. Thus these research needs, as summarized for this workshop, should be evaluated again at a later time.

Transport of chemically dispersed oil at the surface is downward, into the mixed layer, where we have a conceptual model that wind and wave induced mixing move the dispersant and any dispersed oil vertically into the water column, and, in general, droplets less than 70-100 μm in diameter do not resurface. Concentration variations are primarily related to surface initial conditions, e.g. oil (x,y, *thickness*, t), chemical dispersant (x,y, *concentration*, t), wind ($x,y,z\text{-}0,t$), and waves (x,y,t). In the subsurface, particularly the deep ocean, vertical mixing is very low, so, inert chemicals put into the water column travel along the density surface with little mixing. The Deepwater Horizon MC 252 well, and much of the U.S. deepwater development, is located along the Louisiana-Texas continental slope. The circulation along the continental slope is complex. These dynamics affect bottom water movement and, thus advection of dissolved constituents and tiny oil droplets (with rise velocities on the order of weeks to months). In the surface mixed layer, droplets less than 100 μm are viewed as too small to rise against the turbulent mixing. In the deep ocean, the turbulence is much less (Ledwell and Hickey, 1995, Ledwell and Bratkovich, 1995, and Ledwell, Watson and Law, 1993).

During the Deepwater Horizon oil spill, dispersants were also injected into the oil plume at the release point into the water column, first from the broken riser and then from the cut riser at 1,500 *m*. During an oil spill response, we do not have near-real-time information on mixing energy, target or actual dispersant-oil-ratios (DOR), the duration of oil-dispersant interactions, dispersant efficiency, oil droplet size distributions, or identification of physically- vs. chemically-dispersed oil available for decision makers. However, analyses and data to date do indicate that much of the transition from the multiphase gas-oil plume to separate oil and gas bubble phases occurred between 1000 - 1300 *m* (Socolofsky *et al.* (2011), see also Yapa *et al.* (2001)). This layer is the subject of continuing reporting from the Joint Analysis Group (JAG, 2010a, b, c), including a summary report to be completed by the end of 2011.

The separation of oil droplets and gas bubbles from the multiphase flow from the well was accompanied by almost complete dissolution of lower molecular-weight-aliphatics (through heptane, McAuliffe , 1987) and lower-molecular-weight aromatics (alkylated benzenes) (Reddy *et al.*, 2011), with more limited dissolution of two- and three-ring aromatics (alkylated naphthalenes, phenanthrenes/anthracenes, and dibenzothiophenes). Camilli *et al.*, (2010) tracked this subsurface plume at depth for over 35 *km*, and literally thousands of water-column samples collected during numerous Response- and NRDA-cruises have provided measurements of BTEX and PAH distributions throughout the water column. Figures 1 and 2 show dispersant indicators (2-butoxyethanol, glycol ethers, and bis-(2-ethylhexyl) fumerate) and selected BTEX and PAH constituents from the public Operational Science Advisory Team (OSAT) and GeoPlatform.gov data sources. Dissolution kinetics rapidly increase as the oil droplet surface-area-to-volume-ratio increases (i.e., as the droplet sizes get smaller). The intention of the subsurface dispersant application was to transition oil mass from larger to smaller droplet sizes. Presumably, if the subsurface injection of dispersants was effective, dissolution kinetics would have been enhanced, but research is needed to develop methods to be able to evaluate effectiveness on a response time-scale.

2. Surface Chemically Dispersed Oil

2.1 Overview of what was known about topic prior to DWH

Research needs related to decision support for the potential application of chemical dispersants have been discussed previously to the DWH oil spill, and many of these remain relevant today. A comprehensive review of oil-dispersant interactions and fate was completed by the National Academy of Sciences/National Research Council (2005), and since then there have been dozens of studies undertaken under the Dispersant Working Group coordinated by the Coastal Response Research Center (CRRC) and sponsored by the CRRC and a number of other agencies and companies (for a detailed listing of previous research recommendations, projects, and sponsors see: CRRC 2006; 2009; and http://www.crrc.unh.edu/dwg/topic_1.html).

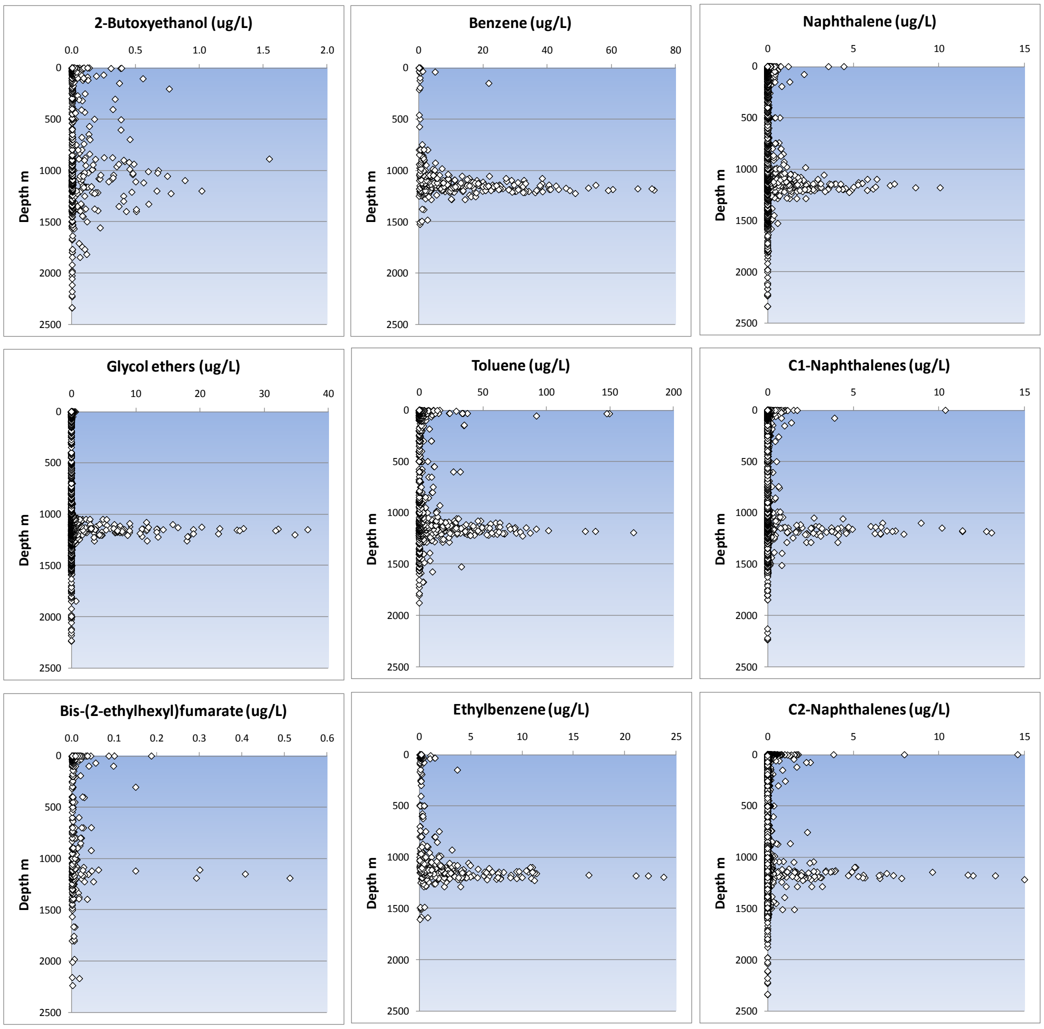

Figure 1. Depth distribution of dispersant indicators (2-butoxyethanol, glycol ethers, and bis-(2-ethylhexyl) fumerate) and selected BTEX and PAH constituents measured in seawater collected throughout the Gulf of Mexico between 11 May and 15 December 2010. [Data source: public Operational Science Advisory Team (OSAT) and GeoPlatform.gov data.]

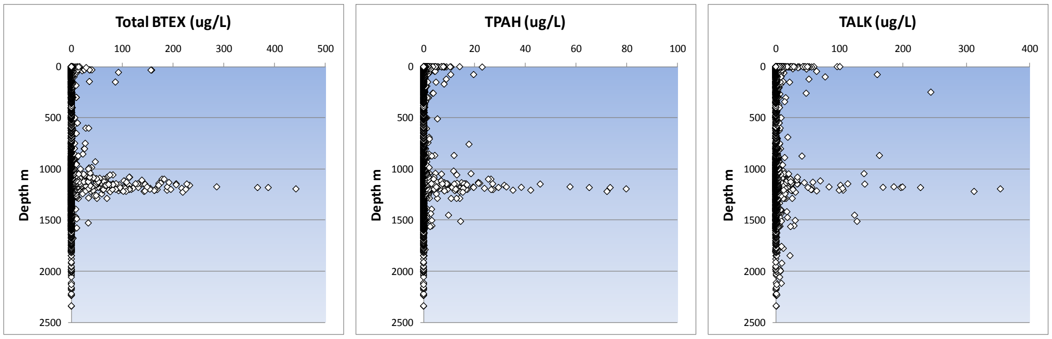

Figure 2. Depth distribution of total BTEX, total PAH (TPAH) and total alkanes (TALK) measured in seawater collected throughout the Gulf of Mexico between 11 May and 15 December 2010. [Data source: public Operational Science Advisory Team (OSAT) and GeoPlatform.gov data.]

During any oil spill response, controlling the source of the oil has a higher priority than research. Access to areas very near the DWH well for sampling was restricted due to response operations. Thus, we have significantly more information about deepwater well blowouts than we did before the DWH oil spill, but research will be needed to develop sampling strategies for areas near the blowout that do not interfere with response activities and that provide more near-real-time information. Innovative research in both technology for direct observations and other chemical and transport proxies that can be used to estimate the droplet size distribution or its properties or derivative (e.g. mass distribution) could improve our ability to operationally forecast more details during a response. As of this writing, however, (1) not all the droplet size data at depth have been characterized, (2) there are operational problems with some of the measurement approaches during the spill (described further below in Section 3.2.1), and (3) these types of measurement need to be more synoptic in order to support response decision activities as compared to longer-term analysis. In addition, the nature of the blowout release(s) likely changed during response activities (e.g. the cutting of the riser between June 1st – 3rd, 2010), which complicates understanding the measurements.

As a result, the observational data from the DWH have yet to be fully leveraged toward answering some or all of these proposed research needs. For example, in the area of dispersed-oil/suspended particulate material (SPM) interactions:

- We have limited data available on SPM concentrations (number density or particle sizes) in the water column at depth close to the wellhead (mid water column or just above the sediments) for subsurface dispersant injection.
- Near-real-time measurements of the oil droplets and SPM for decision support evaluation would have been important near the site of the dispersant injection (at depth), and yet these types of measurements were impossible due to the response activities as noted earlier. The closest most of the scientifically-based ROV platforms could get to the wellhead at depth during response operations was 1-2 *km*, although Reddy *et al.* (2011), were able to mount an isobaric gas-tight sampler on the *Millennium 42* ROV during the response to obtain gas and oil samples immediately above the wellhead on 21 June 2010.
- Post spill sediment core analyses near the wellhead (<2-4 *km*) have shown DWH oil in the upper sediment layers (0-3 *cm*) suggesting oil/SPM interactions, flocculation, and sedimentation, but not all the available sediment cores have been analyzed as of this writing, so our understanding of oil/SPM agglomerate deposition may expand as more information becomes available. In addition, some of the sediment samples also contain drilling mud (possibly related to the Top Kill operations), and drilling mud-oil interactions would also contribute to the sediment load near the wellhead.

Other topics are addressed throughout the rest of this paper. Some topics are addressed in more detail than others, depending on the extent of our pre-DWH knowledge base). Unfortunately, the NRC (2005) report did not address transport issues in any detail.

2.2 Factors influencing:

2.2.1 Chemically dispersed oil droplet size distribution

Droplet size distributions from premixed dispersant/oil mixtures were reviewed in the NRC (2005) report, and since then additional work on surface treated- and untreated-oil has been completed in wave-tank and laboratory studies by Li *et al*., (2007), Lee *et al*., (2009), Khelifa *et al*., (2008), Reed *et al*., (2009), and Katz (2009). Katz has completed the most in-depth investigation of the mechanism of dispersed oil droplet shearing and droplet fractionation. Droplet size distribution is discussed in more detail in Section 3.2.1.

2.2.2 Sedimentation, mucus adherence, and other physical scavenging

The most recent, extensive, and thorough laboratory investigations of chemically and physically dispersed oil/suspended particulate matter (SPM) interactions were completed by Khelifa *et al*. (2008). A number of additional research needs are discussed in that report and in CRRC Workshop documents, but as noted earlier in Section 2.1, not all the new information from the DWH oil spill is available at this time.

Oil droplets (ranging from 20-200 *µm*) were observed by photo microscopy to accumulate in mucus agglomerates collected by bucket casts 5-70 *km* from the wellhead (J.R. Payne, personal observations), and these generally exhibited near neutrally buoyant behavior residing just below the air-water interface. One possibility is that these were from extra-cellular exudation products from bacterial activity, but we do not yet know if this can be addressed from the available samples. Likewise, we do not yet know if we can discern whether or not these mixtures had been previously treated with dispersants.

Another mechanism for getting oil to the bottom includes ingestion of oil droplets by copepods and excretion of basically unaltered oil within fecal pellets (NRC 2003). While much of this material can be re-worked as these fecal pellets settle through the water column, some fraction of this oil is also subject to sedimentation. Methods are needed to assess the relative contribution of this mechanism versus others as it relates to oil deposition on the bottom.

2.2.3 Dissolution

Lower molecular weight aromatics (benzene, toluene, ethylbenzene, xylene(s) – BTEX), and other alkylated benzenes along with lower-molecular-weight polycyclic aromatic hydrocarbons (PAH) have finite solubilities in seawater, and can dissolve to an appreciable extent during an oil spill (NRC 2003, 2005). For the PAHs, the solubility decreases with increased alkylation, such that truly dissolved PAH distributions often do not resemble the fingerprint pattern in the starting oil. Likewise, lower molecular weight aliphatics (methane through heptane) can truly dissolve to varying degrees (decreasing as the molecular weight increases). These processes have been reviewed in detail in several National Research Council reports (2003, 2005), and more recently by Faksness (2007). Successful addition of dispersants will reduce the oil droplet size, and this will significantly increase the oil surface area-to-volume ratio, which will increase the kinetics or rate of the dissolution process.

In the case of the Deepwater Horizon oil spill, the release was at depth so the oil droplets resulting from both physical and chemical dispersion rose in and, for the largest droplets, through the water column. During this contact with the ambient seawater, significant levels of BTEX and PAH dissolved and were measured in hundreds of filtered water samples taken at depth (Figures 1 and 2). Similar behavior was observed during the IXTOC I blowout in the Bay of Campeche, GOM in 1979 (Boehm and Fiest, 1982; Payne *et al.*, 1979a, b). The airborne measurements by Ryerson *et al.* (2011) support these conclusions for the Deepwater Horizon well blowout. The influence of subsurface dispersant injection on this process is considered further in Section 3.3.3.

2.2.4 Droplet Re-coalescence

A comprehensive review of the tendency of dispersed oil droplets to resurface has been prepared by Fingas (2005), and re-coalescence of dispersant-treated oil in OHMSETT Wave Tank studies has been reported by Payne (2006). In the OHMSETT test tank, some resurfacing was observed after 12-24 *hrs* when the wave generator was turned off and turbulence was allowed to dissipate from the system. In those instances, however, re-coalescence primarily occurred after turbulence was reduced or stopped, and it was affected by the lack of advective removal of the dispersed oil in the test tank. In the open ocean, there is unlimited dilution available, and even modest turbulence from surface cooling is enough to introduce sufficient turbulence to maintain small (< 70-100 *µm*) droplets in suspension in the surface mixed layer. The DWH deep submerged plume (1000-1300 *m*) data show no evidence to suggest that any re-coalescence of dispersed oil occurred in the water column as the plume moved away from the wellhead. We expect this to be true from normal advective-diffusive behavior and our understanding of tracer movement within the deep ocean (Ledwell and Hickey, 1995, Ledwell and Bratkovich, 1995, and Ledwell, Watson, and Law, 1993).

2.3 Weathering of dispersed oil

Chemically dispersed oil droplets are subject to the same weathering phenomena (evaporation, dissolution, and microbial degradation) as physically dispersed oil droplets, except the rates would be expected to be higher after successful dispersant application due to the higher surface-area-to-volume ratio of the smaller droplets. Reports indicate that when dispersant-treated oil surfaces the slicks formed are thinner compared to untreated oil. If this is indeed the case, then evaporative weathering would be expected to be faster from such slicks. To the extent that dispersant treatment and enhanced dispersion throughout the water column reduces droplet re-coalescence and surfacing, dispersed droplets would likely not form stable water-in-oil emulsions (mousse) to the extent that non-treated slicks do. Water-in-oil emulsification only occurred with DWH oil after considerable surface weathering (Belore *et al.*, 2011, Leirvik *et al.*, 2010a, 2010b, and Daling *et al.*, 2011) and convergence of oil in Langmuir cells with near-surface wave turbulence. Thus, if dispersed oil remains at depth and diffuses in three dimensions, less oil will be available at the surface for the emulsification process. To the extent that any subsurface chemically dispersed oil eventually does reach the surface, however, it is likely that once the surfactant components have leached out, the oil will be subject to the same convergence cells, photochemistry, and surface turbulence as non-treated oil only with the considerations of having lost more lighter oil components due to higher dissolution. Under these conditions, subsurface chemically-dispersed oil would likely form an emulsion (if this oil surfaces) just as readily as non-treated subsurface released oil.

2.4 Photolytic factors and rates

We are not aware of information that advances our knowledge about the rates and effects of photolysis on chemically-dispersed oil droplets, but presumably the chemically dispersed droplets are subject to the same photo-oxidation reactions as non-dispersed oil if they are near the water surface (~ upper 5 *m*) where UV light penetration is sufficient to catalyze photochemical reactions (Payne and Phillips, 1985, NRC 2003; Maki *et al.*, 2001). In this case, non-chemically-dispersed surface oil would probably be subject to increased rates of photolysis compared to chemically-dispersed oil at greater depths.

Numerous toxicity studies have been completed to assess photo-enhanced toxicity (also reviewed in NRC 2005), and it is well established that selected PAH absorbed into transparent organisms (eggs and larval fish) can impart 10-1000 fold increases in toxicity when exposed to UV light (Barron, 2000; Barron and Ka'aihue 2001; Barron *et al.*, 2002). Similar photo-enhanced toxicity was noted in herring eggs with the same PAH loadings (with either naturally or chemically dispersed oil), but to the extent that dispersants decrease oil droplet size and enhance dissolution, this could increase the potential uptake/partitioning through cell membranes into lipophilic eggs and larvae. Such transport could lead to enhanced phototoxic effects in near-surface transparent organisms where dispersants were used.

2.5 Transport in the Mixed Layer

2.5.1 Slick to droplet continuum

The conceptual model of surface chemically applied dispersant is that the mixing energy from waves (above a minimal energy) in combination with the chemical dispersant leads to smaller droplets. These droplets then move down into the mixed layer through Langmuir Circulation (LC). In shallow areas, $z < 40$ *m*, with steady winds, the resulting LC can reach the bottom (e.g. Gargett *et al.*, 2004).

2.5.2 Langmuir Circulation

In 1999, NOAA and BOEMRE (then MMS) jointly sponsored a workshop on Langmuir circulation (LC) and oil spills, in order to bring experts from both fields together. The results of the workshop were published in a special issue of Spill Science and Technology (volume 6, issues 3-4) in 2000. The workshop recommendations (Simecek-Beatty and Lehr (2000)) focused on LC modeling needs for response based on information that could be obtained during a response, such as mixed layer depth, wind, and waves. Mixed layer depth is a proxy for the depth of penetration of the largest LC, while wind and waves provide the forcing, and so could be used as a proxy for LC intensity. This is more a bulk mixed layer approach. The special issue also included a detailed bibliography (Simecek-Beatty and Overstreet (2000)).

LC is found at all scales within the ocean mixed layer. Colbo and Li (1999) did a very nice study on particle dispersion in LC, showing that particles tended to move within individual Langmuir cells, with the smallest cells persisting over a much smaller time period than the larger cells. By comparing buoyant and neutrally buoyant particles within LC, they showed that buoyant particles do not disperse (spread) as much in the cross-wind direction as neutrally buoyant particles.

Thorpe (2004) noted in a review of LC noted that LC simulations using Large Eddy Simulation (LES) methods was a great step forward in terms of understanding mixed layer dynamics. LES models of the mixed layer could be used to develop more detailed statistics for oil droplet dispersion within LC, and thus may be able to give statistical information on hydrocarbon concentrations that could be used in oil spill models. We expect this to result in details of small volumes of higher hydrocarbon concentrations than the overall concentration estimates from bulk methods. Transitioning this type of work into decision support materials or models is also a significant effort to undertake.

2.6 R&D Recommendations

2.6.1 Overview of NRC and/or CRRC R&D recommendations prior to DWH

UNH CRRC (2009). "Research & Develop Priorities: Oil Spill Workshop, March 16-19th, 2009.

Chemical Dispersion
"The research will require meso-scale and, full-scale field trials that include tracking and monitoring techniques. Other guidelines include investigating cold water environments, and multiple oil (including heavy) and dispersant types. Potential impediments to research are public perception and politics, the difficulty of control, the limited scope, and the expensive field trials."

2.6.2 Post DWH oil spill

See sections 3.6.2 and 3.6.3.

2.6.3 R&D needed to resolve outstanding questions relative to topic

Below is a summary of the research needs from the 2005 UNH CRRC dispersant workshop (with a current status estimate by the authors in parentheses):

- Literature synthesis on physical and chemical properties of oils that determine the overall effectiveness of dispersant application (largely completed);

- Refining existing datasets to correlate physical and chemical properties of different types of oil with dispersability (ongoing);
- Update SMART monitoring protocols;
- Workshop on requirements for integrating oil toxicity and biological data with oil fate and transport models;
- Improved models to predict dispersant effectiveness and oil fate;
- Understanding the interactions of chemically dispersed oil droplets with suspended particulate matter (largely completed) and how these processes affect the rate of oil biodegradation and ultimate fate of dispersed oil (ongoing);
- Assessment of the degree, rate, and consequences of surfactant leaching from surface slicks and chemically dispersed oil droplets;
- Reconciliation of the differences between the empirical evaporation approach and traditional pseudo-component approach;
- Improve, verify, and validate oil-spill trajectory and fate models;
- Monitoring dispersed oil concentrations at spills of opportunity; and
- Integration of fate and toxicity models with population models to predict short- and long-term effects of dispersant application.

3. Subsurface Chemical Dispersant Application as Applied During the Deepwater Horizon Oil Spill

3.1 Overview of what was known about topic prior to DWH

The authors are not aware of any published evidence that subsurface dispersant application was considered for deepwater well blowouts or other response scenarios before the DWH oil spill, though at the workshop, industry indicated consideration as early as 2000. The BP Thunder Horse deepwater well riser break, which was a dry run for response considerations for the DWH oil spill, is discussed in Beegle-Krause and Lynch (2004). Modeling and response considerations for deepwater well blowouts previously focused on the timing and location of the surface oil expression.

3.1.1 Conceptual model

For subsurface dispersant application, our conceptual model is that by injecting chemical dispersants into the blowout multiphase plume, the inherent mixing from the blowout would lead to oil-dispersant contact and creation of more smaller oil droplets (*i.e.* transition a portion of the mass from larger to smaller droplet sizes). The fluid emerging from the wellhead is not a mixture of oil and gas separately but multiphase flow, which means that the oil and gas emerge as a single phase. Unfortunately, while overflight data support the notion that the freshest surface oil slick decreased in size when subsurface dispersant application was on-going, tracing the oil droplets creating the surface oil back to the riser with and without dispersant injection was not possible in real time for response decision makers. Ryerson *et al.* (2011) used aircraft measurements of promptly evaporating hydrocarbons to evaluate the area of freshest oil with a measureable atmospheric hydrocarbon signal.

The blowout scenario likely changed (e.g. droplet size distribution) with the various response options, particularly when the riser was cut. This is evidenced by the change in the isopyncal expression of the subsurface plume over time (Socolofsky *et* *al*., 2011 and JAG final report to be published). Kujawinski *et al.* (2011) found the evidence of dispersants within the depth range of the subsurface plume, but not enough information on the exact isopycnal location of the Dioctyl Sulfosuccinate Sodium Salt (DOSS) was provided to determine the detailed relationship between the DOSS and the CDOM fluorescence. For example, did the DOSS occur at the same density level as the peak CDOM fluorescence or throughout the layer? Elsewhere, the correlation of subsurface dispersant components and dissolved/particulate-phase oil was observed (e.g., Figures 1 and 2), and this is discussed further in Section 3.3. In addition, it would be interesting to compare the mechanical frictional effects of the broken riser leaks to create smaller droplets (e.g. picture your thumb over the flow from a garden hose) to the efficacy of the subsurface chemical dispersant application. There is potential that mechanical dispersion could be utilized to replace subsurface chemical dispersant usage.

3.2 Factors influencing:

3.2.1 Droplet size distribution

Droplet size measurements were completed as part of the DWH response effort to inform Command and Control of dispersant effectiveness (Li *et al.*, 2011) and as a component of several NRDA-cruises completed in the spring, summer, and fall of 2010. Unfortunately, very few of the Laser *In Situ* Scattering and Transmissometry (LISST) instruments used at the time of these studies were capable of reaching the depths necessary to monitor droplet sizes *in situ*. Therefore, most measurements were completed on water samples collected at depth (with Go Flo or Niskin bottles) and then returned to the surface for analyses on the ship(s). SINTEF is currently undertaking new research on oil droplet size and size distribution using tower basins.

With this approach, oil-droplet coalescence can occur inside the water sampling bottles during the 1-3 *hr* period between sample collection at depth, retrieval of the sampling equipment, and analysis of the water sample on the ship. Oil sheens were frequently observed on the upper surface of the standing water in Go Flo bottles on the *Jack Fitz* NRDA cruises, and special care had to be taken during water filtration using the Portable Large Volume Water Sampling System (PLVWSS – Payne *et al.* 1999) to ensure that the surface meniscus (containing such oil sheens) was processed as part of the sample. This was not possible with LISST measurements because there is no way to get the surface-separated oil in the sampling bottles back into suspension as finite droplets, and there is no guarantee that the droplet size distribution would be the same as it was at depth. Also, as the water samples warm up in the flow-through chambers or cuvets used with the LISST instrumentation, degassing can cause air bubbles to form. Both of these issues (recoalescence in the sampling bottles and air bubbles) need to be considered when accessing the accuracy of droplet size measurements for response decision support.

To avoid these issues, additional instrumentation including an *in situ* Holographic Camera and towed video-cameras designed to measure droplets, suspended sediments, and plankton (owned by Cabell Davis, WHOI) were deployed on a number of cruises, but data from these systems are not yet available at the time of this writing. Likewise, a Deep-LISST capable of reaching the bottom at 1500 *m* was deployed on several NRDA cruises, but those data are also not available at this time.

3.2.2 Sedimentation

As indicated in section 2.2.2, laboratory studies have demonstrated that chemically dispersed oil droplets can interact with suspended particulate material (SPM) in the water column to yield oil/SPM aggregates that have densities high enough to cause enhanced sedimentation. During the DWH oil spill, settling chambers were deployed to measure flux of oil-laden SPM to the bottom, but at the time of this writing the results from those studies are not yet available. Furthermore, specific studies to differentiate oil droplets created from subsurface dispersant injection have not been put forward.

The OSAT summary report on subsurface oil and dispersant detection (OSAT 2010) identified DWH oil in seven sediment samples within 3 *km* of the wellhead, but the samples were composites of the upper 3-plus *cm* of the sediment, so background PAH contributed to the signal and could have masked and underestimated the DWH contribution to the surface layer. In addition, the primary focus of the OSAT report was on actionable levels above aquatic life benchmarks for PAH (with oil concentrations > 2000-5000 *ppm*) for making response decisions. The OSAT authors were quick to point out that these indicators do not represent injuries to natural resources under NRDA, which may occur at lower concentrations, and in other studies, DWH-sourced oil has been measured in sediment and surface floc samples at distances out to 4 *km*. Preliminary reports on hydrocarbon fingerprinting of publicly available data (Scott Stout, verbal communication) indicated DWH oil in the surface sediment (0-1 *cm* and 1-3 *cm*) and DWH oil in surfacial floc samples, so it is believed that oil/SPM interactions and sedimentation has occurred. Our expectation is that this type of information during response would be useful for decision makers. We expect that ongoing studies will provide additional data to possibly ascertain if these interactions occurred with dispersant-treated oil, but for future response we need to have a better understanding of the formation mechanisms.

3.2.3 Dissolution and evidence of dispersant effectiveness at depth

Dissolved components (methane through pentane, plus BTEX) were reported by Camilli *et al.*, (2010) and Reddy *et al.* (2011), and dispersant components plus BTEX and PAH were measured in thousands of water samples collected as part of the Response and NRDA efforts (Figures 1 and 2). Three dispersant indicators (2-butoxyethanol, generic glycol ethers, and bis-(2-ethylhexyl) fumerate) and numerous oil components are observed to be co-located between ~750 and 1500 *m* (Figure 1). While all three dispersant components were readily observed (and all are water soluble), we have more data for the glycol ethers, so additional discussions regarding dissolution behavior presented below will focus on them.

The BTEX components are known to be primarily in the dissolved phase (Reddy *et al*., 2011), but the higher-molecular weight PAHs have variable water solubilities, and n-alkanes (C_9-C_{40}) are known to exist only in the oil phase (finite oil droplets) or very fine colloidal fractions. Thus, from the data in Figures 1 and 2, it is clear that the subsurface oil plume contained both truly dissolved components and finite oil droplets. From the available data at this time, further analysis is needed to know if we can definitively determine whether or not the dispersants shifted the droplet size distribution toward smaller droplets. At this time, analysis of available deep oil droplet data has not yielded any dispersant components associated with the oil, but there are data from many samples remaining to be examined. Preliminary analyses from Fisheries and Oceans Canada (Ken Lee, personal communication) indicates a transition of Volatile Organic Compounds (VOCs) between the surface and deep subsurface layer that correlates with subsurface dispersant application.

Before considering that point further, however, it is first necessary to discuss the fate of the detrained oil droplets as the smallest (presumably colloidal sizes up to possibly up to several hundred µm) are advected horizontally while the larger (*mm* plus) sized droplets rise much more rapidly (hours) up through the water column.

During the NRDA water sampling activities on three *Jack Fitz* cruises (May-June 2010), the first *American Diver* cruise (August 2010), four *HOS Davis* cruises (August – December 2010), and the first two *HOS Sweet Water* cruises (March/April and July/August 2011), water column samples were processed with the Portable Large Volume Water Sampling System (PLVWSS) developed by Payne *et al.* (1999) to allow examination of separate dissolved- and particulate/oil-phases. Data from five discrete depths are available for most samples, but only data from 1 *m*, 600 *m*, and 1430 *m* collected 2.2 *km* from the wellhead are presented here (Figure 3) due to space limitations. Each depth is represented by four histogram plots vertically arranged to show PAH components above the corresponding alkane (or aliphatic – ALK) components in each sample. The dissolved-phase samples (passed through a 0.7 µm glass-fiber filter at the time of collection) are shown in the left-hand column, and the particulate/oil-phase samples (retained on the filters) are shown in the right-hand column. The red line in each PAH plot is the profile of the DWH source oil normalized to the C-2 phenanthrene (C-2P) in each plot. The red line in each ALK plot is the relative distribution of the alkanes plus pristane and phytane, but they are not normalized to any specific component in the sample.

The data very clearly illustrate the enrichment of parent and alkylated naphthalenes, fluorenes, and phenanthrenes in the aqueous phase (compared to the starting oil) with concomitant depletion of these same components in the particulate/oil phase trapped on the respective filter obtained with each sample (compare PAH profiles in the left- and right-hand columns). Likewise, the insoluble n-alkanes and isoprenoids are almost exclusively found in the particulate/oil phase trapped on the filters (right-hand column).

Figure 3. Paired dissolved (left side) and filtered particulate/oil-phase (right side) PAH and alkane (ALK) profiles from water depths of 1m, 600m, and 1,430 m collected 2.2 km (1.3 mi) to the NW (bearing 330 degrees) from the wellhead on 28 June 2010. The red PAH line is fresh DWH oil normalized to C2-phenanthrene showing enhanced dissolution of lower-molecular-weight PAH in the dissolved phase (left-hand column) and depletion of these same constituents in the particulate/oil-phase (right-hand column). Higher-molecular-weight aliphatics (alkane – ALK) are only observed in the particulate/oil-phase (see text). [Data source: Publicly available data from GeoPlatform.gov.].

Correlations of glycol ethers with specific components (BTEX and PAH) as a function of the depth range of the collected samples (Figures 4 and 5) also can be used to better define the plume dynamics. In Figure 4 for all water depths, good correlations are observed between the glycol ethers and the more water soluble constituents (BTEX through C2-naphthalenes), but the correlations break down for the lower soluble fluorene, phenanthrene and dibenzothiophene suggesting separation of the dissolved components from the finite oil droplets as they rise through the water column. In Figure 5 for water depths only between 750 *m* and 1500 *m*, the correlations are more significant for all of the constituents.

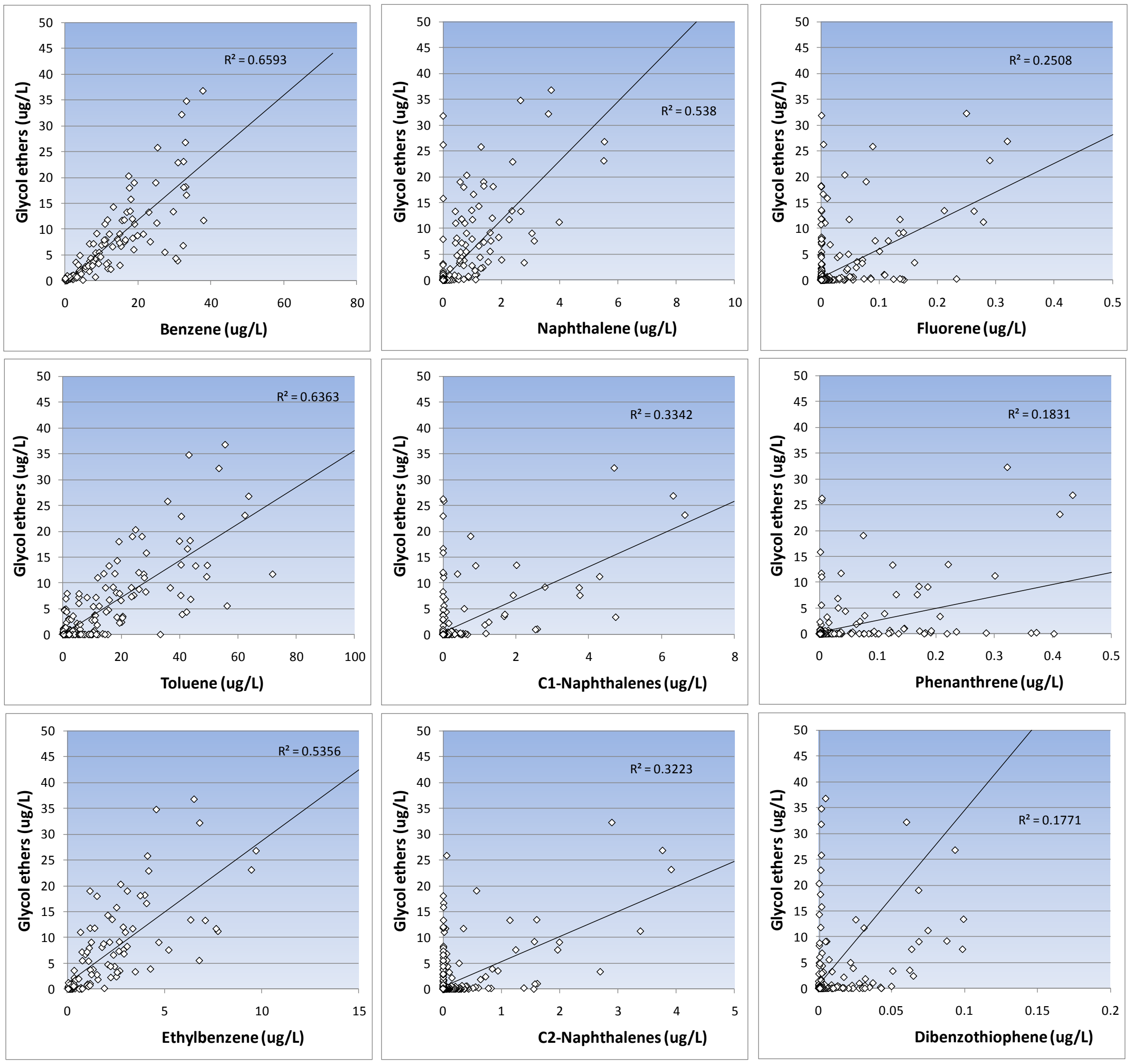

Figure 4. Glycol ethers vs. individual BTEX and PAH constituents in water samples from all depths collected throughout the Gulf of Mexico between 11 May and 15 December 2010. [Data Source: publicly available data from GeoPlatform.gov.].

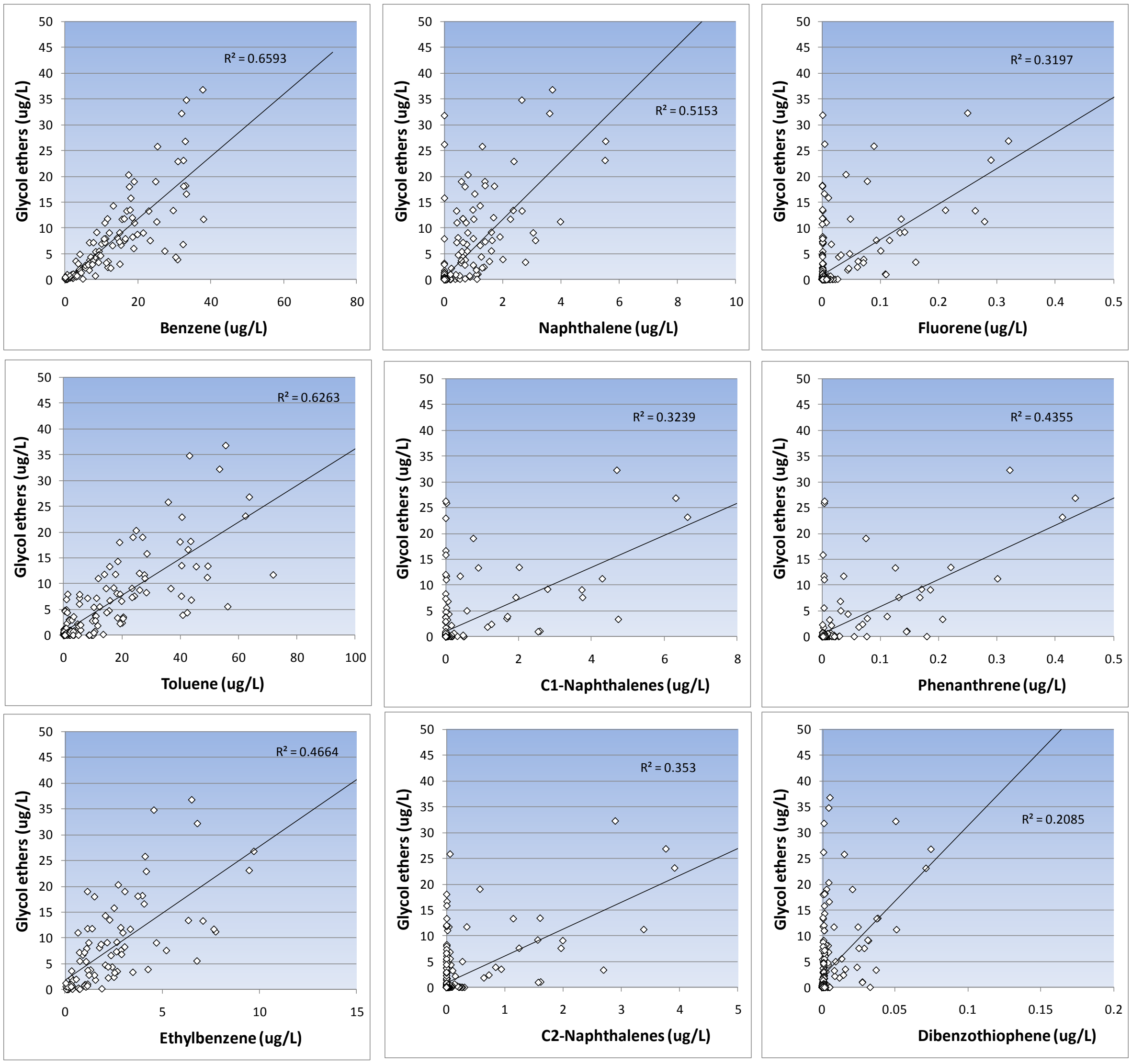

Figure 5. Glycol ethers vs. individual BTEX and PAH constituents in water samples between depths of 750 and 1500 m collected throughout the Gulf of Mexico between 11 May and 15 December 2010. [Data Source: publicly available data from GeoPlatform.gov.].

3.2.4 Re-coalescence

As part of response, USCG SMART water sampling protocols were employed during the DWH surface dispersant applications (Levine *et al.* 2011), but no data to date have been presented to assess droplet re-coalescence and resurfacing. When dispersants were applied by air, the observation vessels were required to stand-by at considerable distance from the target area for safety, and when they approached the dispersant-treated slick, the logistics were challenging to ensure that the SMART teams were exactly within areas of surface dispersant application. It may have been advisable to deploy drifters and/or smoke markers in the target areas before dispersant applications by air as described in the California Dispersed Oil

Monitoring Plan (Payne *et al.*, 2007a,b; 2008a,b; French McCay *et al.*, 2007; 2008a, b), but that approach is more suited to oil-spill-of-opportunity research rather than operational sorties in response to a spill of the magnitude of the DWH.

3.3 Biodegradation of dispersed oil

At the time of this writing, further analysis is needed to determine if biodegradation of subsurface chemically-dispersed oil is the same as the smallest oil droplets created by the subsurface blowout dynamics. Studies of microbial degradation of dissolved oil are ongoing and being published, for example: Hazen *et al.*, 2010, and Reddy *et al.*, 2011. Other weathering considerations were presented in Section 2.3. The DWH subsurface layer transitioned from dissolved oil and gas and the smallest oil droplets into a dissolved oxygen depression (or "anomaly"), that research indicates to be from microbial degradation of the oil at depth. This dissolved oxygen (DO) anomaly has been discussed extensively by the JAG (JAG 2010a, b, c), with the final JAG report expected to be published at the end of 2011.

3.4 Transport in the Deep Ocean

Consideration for the subsurface transport of chemical dispersant and any resulting chemically dispersed oil are very different from the surface. At the surface, application is at the air-water interface, where the oil resides at the interface, wind and waves supply the mixing energy, and dispersed oil and chemical dispersant mix downward into the surface mixed layer. In the subsurface, mixing is greatly reduced compared to the surface, so persistent chemical tracers can be found for long periods of time. For example, the work of Ledwell and Hickey, 1995, Ledwell and Bratkovich, 1995, and Ledwell, Watson and Law, 1993 using sulfur hexafluoride has shown that an inert tracer can injected into the subsurface ocean can be found again over a course of years. Transport in the horizontal is along constant density surfaces ("isopycnals"), which are roughly the same as depth levels, but not exactly. The upcoming final JAG report and Beegle-Krause *et al.* (2011) show and discuss the key isopycnals for the DWH MC 252 oil spill.

Kujawinski *et al*. (2011) collected and published data on deep water samples that contained very low concentrations of DOSS from the chemical dispersant (see also Figures 1 and 2). Kujawinski et al. (2011) provided information on the long-term horizontal transport of the DOSS, but, as noted in the paper, not on the efficacy of the subsurface dispersant application. Further water mass and other analyses could potentially complement chemical analyses in understanding the effectiveness of subsurface dispersant application.

3.5 Dispersed oil transport

Due to isopyncal transport in the deep ocean, water-soluble dispersant components would be expected to follow the isopyncal where they entered the larger scale environment. Smaller chemically-dispersed oil droplets would be expected to travel similarly to any dissolved species in the deep water column, although larger (> 100 μm) droplets might slowly rise over time.

3.6 *R&D Recommendations*

3.6.1 Overview of NRC and/or CRRC R&D recommendations prior to DWH (Are these still relevant post-DWH?)

The NRC and UNH CRRC have not previously considered research needs for potential subsurface dispersant application.

3.6.2 Overview of R&D recommendations post DWH oil spill

With new response measures come new R&D recommendations to help us better understand the effectiveness and potential effects of using these new measures in the field. Below some examples:

- Could a frictional/mechanical oil droplet dispersion method be more effective at creating smaller droplets than the subsurface application of chemical dispersant?
- How effective is application of subsurface dispersant in creating more small droplets? What specific dispersant injection methods (and/or orientations relative to the plume) are necessary to accomplish various degrees of effectiveness? Does dispersant use affect dissolution as oil particles rise to the surface or change the gas bubble size distribution? How long does the surfactant stay with the dispersed oil droplets?
- Can subsurface injection of chemical dispersant reliably reduce the amount of oil reaching the surface? If so, what are the most effective injection methods? Can dispersant formulations be optimized for subsurface use?
- How would we better measure subsurface chemical dispersant effectiveness during the next event?
- How do these processes affect biodegradation kinetics, composition of sedimented oil, and the ultimate fate of dispersed oil?
- Can SMART Protocol improvements be developed to allow better tracking of dispersed oil at depth? For example, can holographic cameras be utilized as a standard component of the Protocol to measure *in situ* droplet sizes at depth?

4. Overall Summary of Response Decision Support Research Needs for Chemical Dispersant Applications

Below in section 4.1 is a summary of post-DWH research needs related to chemical dispersant decision support discussed within this paper. A separate addendum is also available that lists a summary of research needs discussed by the Fate and Transport working group at the CRRC Workshop. Many of these are significant efforts to undertake, so research needs and results will have to be reevaluated again at a later date. See section 2.6.3 for the pre-DWH outstanding dispersant decision support research needs summary.

4.1 *Overall Summary of Post-DWH Research Needs for Response Decision Support*

- Can mechanical methods be developed to increase the oil mass within the subsurface layer that are more (or at least as) effective as chemical dispersants?

  - The effectiveness of mechanical dispersion (friction from riser kinks and brakes and post-riser-cut) should be evaluated so as to compare with the effectiveness of subsurface chemical dispersant application.
- We need to transition our understanding of surface dispersant application and effectiveness to the specific case of a deepwater well blowout. Topics/data needs include:
  - Evaluation of our understanding of the mechanism of dispersed oil droplet shearing and droplet fractionation under subsurface conditions.
  - Evaluation of emulsion stability for surface oils previously weathered by dissolution (e.g. surface oil slicks created from droplets rising from a deepwater well blowout) with and without the application of subsurface chemical dispersants.
- What methods and protocols could be used to determine effectiveness of subsurface chemical dispersant application for decision support? Topics/data needs include:
  - Measurements to support detailed water mass analysis of oceanographic and oil spill related chemical parameters.
  - Measurements of mixing energy, target or actual dispersant-oil-ratios (DOR), the duration of oil-dispersant interactions.
  - Measurements of dispersant components within oil droplets (as isolated from the dissolved phase by the Portable Large Volume Water Sampling System (Payne *et al.*, 1999).
  - Measurements of droplet size distribution and temporal variance.
  - Near-real-time measurement systems that can work near a deepwater blowout well without interfering with response activities or near-real-time proxies that can be measured outside the response exclusion zone.
  - Quantitative near-real-time evaluation of the footprint (x,y,t), mass(t) and chemical composition (x,y,t) of the freshest surfacing oil.
- What is the role of physical scavenging (oil/SPM interactions) in chemical dispersant application and effectiveness (surface and subsurface)? Topics/data needs include:
  - Spatial and temporal (x,y,z,t) background, natural variance, and near-real-time SPM concentrations (number density or particle sizes) in the water column.
  - Near-real-time measurement systems that can work near a deepwater blowout well without interfering with response activities or near-real-time proxies that can be measured outside the response exclusion zone.
  - Protocols for decision support evaluation of mucus agglomerates for chemical signatures of dispersants or byproducts of biological interaction with dispersant components or dispersed oil droplets.
  - Protocols for decision support sediment core analyses near the wellhead (<2-4 *km*) in the upper sediment layers (0-1 *cm*) for evidence of dispersant effects, e.g. oil/SPM interactions, flocculation,

    - and sedimentation, fecal pellets containing dispersant products, and other response related chemical constituents (e.g. drilling mud).
    - Detailed analysis of SPM interactions with oil droplets.
    - How these processes affect biodegradation kinetics, composition of sedimented oil, and the ultimate fate of dispersed oil.
- How can SMART Protocol improvements be implemented to provide:
    - Better positioning of the SMART team into the surface chemically dispersed oil for sampling.
    - Measurements to estimate droplet re-coalescence and resurfacing.
    - Tracking and sampling of dispersed oil at depth.
    - Aerial documentation of the surface manifestation of oil that can be quantitatively compared with the subsurface dispersant application.
- Are the effects of photolysis the same on chemically- and physically-dispersed oil droplets?
- Prepare post DWH guidance documents for:
    - Decision makers on effects of chemically dispersed oil.
    - The scientific community on oil-related sampling equipment, standard analyses, and fingerprinting.

5. Relationship of R&D recommendations & Arctic dispersant use

The risks of potential well blowouts are real in any oil development. The arctic and Gulf of Mexico scenarios for oil spills are very different.

5.1 Surface oil

Ice conditions are a key consideration to surface dispersant application to oil in the Arctic. The DWH oil spill is an example of very high volumes of dispersant applied in an effort to improve the outcome from the oil spill in very deep water. Consideration in detail of the potential for a well blowout in the Arctic and application of dispersant should be done carefully, as lessons learned from the DWH oil spill may not all apply to the Arctic.

5.2 Subsurface oil

Oil development within the Arctic is expected to be at much shallower depth than the deepwater development that included the DWH. These shallower depths may point to blowout events behaving more like the IXTOC I exploratory well blowout than the DWH. The ability to potentially manipulate the subsurface release or apply subsurface dispersants exists, but needs further consideration relative to the Arctic ecosystem.

6. Summary

The needs of response are higher than the needs for research – this is an important trade-off to recognize when evaluating previous observational programs under the DWH and considering future research needs. The DWH oil spill resulted in an unprecedented oil spill data set that can be used to improve our response capability should another deepwater well blowout occur. Nevertheless, there are still areas where research could advance our understanding and predictive ability regarding deepwater well blowouts.

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Biological Effects of Dispersants and Dispersed Oil on Surface and Deep Ocean Species

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INTRODUCTION

Effects of Dispersant Use on Biological Systems

Beginning with the use of industrial-strength detergents, dispersing agents have been employed in spill response for decades. The Corexit series of agents in common use today generally consist of non-ionic and/or anionic surfactants in a solvent base designed to enhance miscibility under varying temperature and salinity conditions; cationic surfactants tend to be too toxic for use. While dispersants generally serve to decrease the interfacial surface tension of oil, thus facilitating its weathering under low-energy conditions, their surface-active nature also causes their interaction with cell surfaces – those of single-celled organisms as well as the gills of vertebrates and invertebrates.

Knowledge from Previous Oil Spills

Biological Impacts

Dispersant use is usually considered by spill responders when other means of response, such as containment and removal, are not deemed to be adequate[1]. For instance, during the Deepwater Horizon (DWH) spill dispersants were quickly employed when it became apparent that other means of response were insufficient[2]. However, there are usually consequences for both hydrocarbon bioavailability and toxic impacts, thus environmental tradeoffs must be evaluated. For instance, while undispersed oil generally poses the greatest threat to shorelines and surface-dwelling organisms, most dispersed oil remains in the water column where it mainly threatens pelagic and benthic organisms[1]. This tradeoff was a prime consideration during the DWH spill[3].

Bioavailability of Oil Constituents

Crude oil consists of hundreds of individual hydrocarbons, both aliphatic and aromatic; water solubility is directly related to temperature but inversely related to molecular mass and salinity[4]. Undispersed oil generates a relatively small particulate fraction, as the bulk of the hydrocarbons remain near the water surface, while dispersion results in the generation of a large particulate fraction, which forms a pelagic “cloud.” Adverse effects resulting from spilled oil can be a result of: (1) dissolved materials, (2) physical effects due to contact with oil droplets, (3) enhanced uptake of petroleum hydrocarbons through oil/organism interactions, or (4) a combination of these factors[5]. Both particulate (via ingestion and surface coating) and dissolved hydrocarbons can have adverse effects[1], but bioavailability is generally defined as the hydrocarbon fraction available for diffusion across cell membranes (i.e. the dissolved fraction). While the intentional dispersion of an oil spill places a larger load of particulate hydrocarbons nearer to pelagic and/or benthic organisms, they are initially contained within surfactant-enclosed micelles and generally unavailable for membrane diffusion. However, over time, the surfactant will dissolve and dissipate.

The bioavailability question in relation to oil dispersal has been addressed for many years, but much of the research has been hampered by a lack of adequate analytical support[1]. Early on, nominal concentrations were often used to characterize exposures, but even more recently characterizing exposure concentrations has been a formidable challenge in regards to the separation of dissolved versus particulate fractions. Recent investigations involving the use of metabolomics have demonstrated that, while traditional bioassays have shown naturally dispersed oil to be significantly more potent than chemically-dispersed oil, metabolic effects are surprisingly similar[6, 7]. Recently, using semi-permeable membrane devices (SPMDs), it was discovered that, while chemical dispersal places more total oil in the water column, dissolved PAH fractions were very similar (Van Scoy, pers. comm., 2011).

Testing/Field-Monitoring Procedures

Methods Used to Assess Impacts from Dispersants and Dispersed oil

Many methods have been developed to assess the impacts from dispersants and dispersed oils over the years. Starting in the 1970s and continuing through the 1990s, the main focus was on Corexit 9527, as it was the primary agent stockpiled for use in the United States[1]. In the 1990s, the focus shifted to the newer Corexit 9500, but as available research funding declined following the Exxon Valdez spill, research efforts concurrently declined.

Early methods focused on ecological impacts and involved field studies following major spills[1]. Most employed commonly-used ecological tools and approaches to determine changes in populations and communities, with an emphasis on migrating offshore surface spills and their impacts on sensitive shallow nearshore water areas (coral reefs, mangroves, etc.) and shorelines (subtidal through intertidal zones). The impacts of deep water well blowouts (such as was observed with the DWH spill) on both benthic and pelagic regions have been little studied, and remain relatively unknown today.

Analytical Chemistry and Toxicity Testing of Dispersants and Dispersed oil

For many years the standard for analysis of crude oil, dispersants and dispersed oil has been gas chromatography equipped with flame-ionization detection (FID-GC)[1]. In recent years mass spectrometry (GC-MS) has replaced FID due to its increased sensitivity and availability. Rapid field analysis has been routinely performed by deploying a specially-equipped fluorometer– which detects fluorescent PAHs at very low concentrations, but is not generally useful in the detection of dispersants.

Toxicity bioassays have been conducted since at least the 1970s, with early methods involving a variety of organisms, open static or serial-dilution exposure systems, and constant concentrations of either dispersants and/or dispersed oil[1]. The varied solubility and vapor pressures of the different hydrocarbons made control of exposure concentrations nearly impossible, thus flow-through systems were developed[8]; they facilitated better control of both constant and declining exposure concentrations, which can better mimic the actions of dilution in the environment[9].

Due to the nearly endless number of permutations in variables modeling natural spill conditions, in more recent years a group of researchers attempted to standardize testing conditions to minimize variability between research groups and make results more directly comparable (reducing the "apples and oranges" problem). Thus, CROSERF (Chemical Response to Oil Spills: Ecological Effects Research Forum) was created. Utilizing the methods of Singer *et al.*[9], CROSERF also sought to standardize a suite of marine test organisms (sensitive early life stages) and the formation of both the water-accommodated fraction of crude oil (WAF, naturally-dispersed oil) and the chemically-enhanced water accommodated fraction of crude oil (CEWAF, via Corexit 9500)[10].

Early test methods involving crude oil and dispersants also reported nominal exposure concentrations, which today are no longer generally acceptable[1]. Bioassays now routinely employ either FID-GC or GC-MS to confirm exposure concentrations. However, due to the difficulty in separating dissolved from particulate oil, exposures are generally characterized by their total petroleum hydrocarbon content (TPH), which may result in the reporting of excessively high median-effect concentrations. Ideally, analytical methods should separately report dissolved and particulate hydrocarbons, but separation methods (centrifugation or filtering) often disturb particulates to produce an unrealistically high dissolved concentration.

STATE OF KNOWLEDGE FROM THE DEEPWATER HORIZON

Several hundred water and sediment samples were collected during the DWH response from nearshore and deepwater areas. The Operation Science Advisory Team (OSAT) analyzed the bulk of these samples to characterize the risk of oil and dispersants to aquatic receptors and humans[11], including samples collected through monitoring missions implemented during the response. Such missions included Special Monitoring of Applied Response Technologies (SMART) and Measurement of Concentration and Size Distribution of Surface and Subsurface Small Particles. Samples were also collected as part of the Natural Resource Damage Assessment (NRDA), but these were not available for inclusion in this synthesis.

Dispersant Indicators in Water and Tissue Samples

The U.S. Environmental Protection Agency (USEPA) established analytical methods and screening levels for selected dispersant-related chemicals in water samples (Table 1). Comparisons of measured versus screening level concentrations were widely used during the response to characterize risks to aquatic receptors[11]. Approximately 28% (2,791 samples) of the 10,000 water samples collected for dispersant analysis were from the area with the highest concentration of dispersant application (Figure 1). In this area, propylene glycol, DPnB, and DOSS were detected in a few samples collected during the surface and sub-surface dispersant application periods (22 April-19 July 2010, and 30 April-15 July 2010, respectively), but none exceeded the recommended benchmarks. The large majority of samples collected at depths >200 m with detected dispersant indicators (89%) were from 1,025 to 1,425 m depths consistent with the location of the subsurface plume (1,000-1,500 m)[12-14].

Dispersants in seafood tissues were analyzed by the Food and Drug Administration (FDA). Laboratory tests with Eastern oyster (*Crassostrea virginica*), blue crab (*Callinectes sapidus*), and red snapper (*Lutjanus campechanus*) exposed to Corexit 9500 (100 mg/L)[15] indicated little to no bioconcentration potential, and depuration from tissues within 24-72 h. DOSS was detected in 4 of 299 tissue samples (concentration range: 0.011-0.1 µg/g) from seafood species collected in State and Federal waters between June and October 2010. Based on the FDA data (low tissue concentrations, low bioconcentration, fast depuration), it is unlikely that DOSS may pose a significant risk to aquatic receptors.

Table 1. Analytical methods and screening levels for selected dispersant-related chemicals in water samples established by the EPA in response to the Deepwater Horizon oil spill (http://www.epa.gov/bpspill/dispersant-methods.html).

Compound	CAS Number	EPA Method ID	Reporting Limits (µg/L)	EPA Aquatic Life Benchmark (µg/L)
Propylene Glycol	57-55-6	EPA SW 846 Modified 8270	500	500,000
2-Butoxyethanol	111-76-2	EPA R5/6 LC	125	165
Di(Propylene Glycol) Butyl Ether (DPnB)	29911-28-2	EPA R5/6 LC	1	1,000 chronic*
2-Ethylhexanol	104-76-7	EPA SW 846 Method 8260	10	NA
Dioctylsulfosuccinate, sodium salt (DOSS)	577-11-7	EPA RAM-DOSS	20	360 acute 40 chronic

*Chronic screening level for DPnB agreed upon by BP and EPA during the DWH response

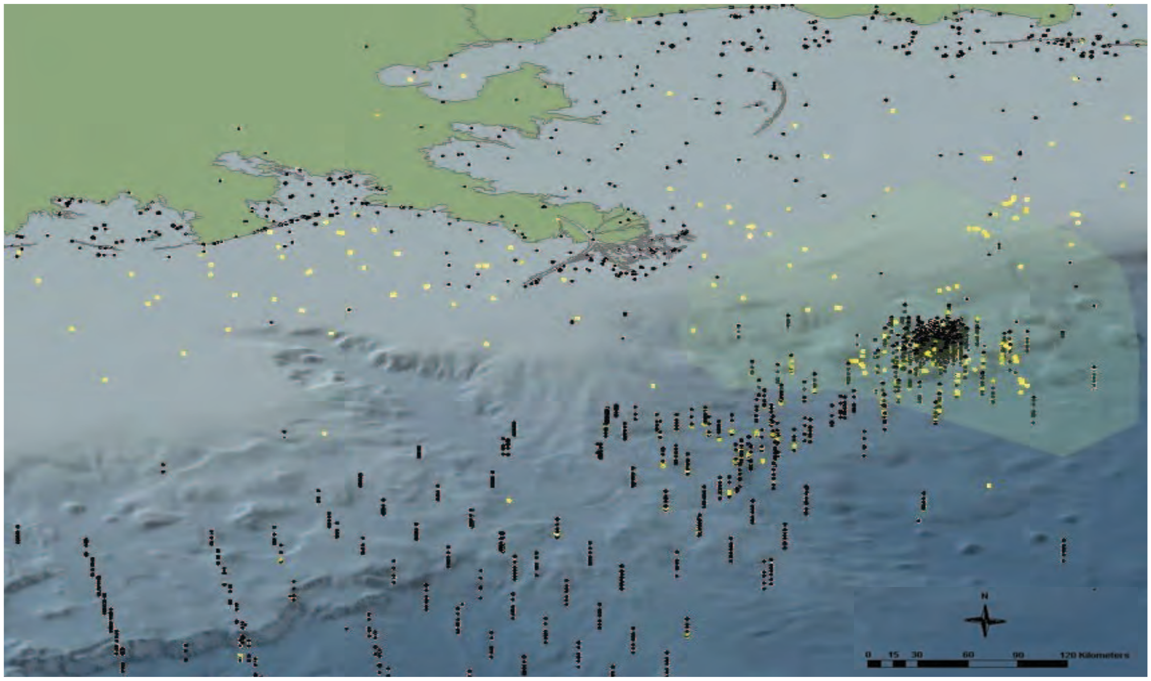

Figure 1. Three-dimensional location of water samples collected for dispersant analysis. The yellow-shaded, offshore-polygon depicts the area with the highest concentration of dispersant application. Black symbols: samples with no detected dispersant-related chemicals; yellow symbols: samples with detected dispersant-related chemicals.

Chemically Dispersed Oil

Response data[11] were used to characterize the potential adverse effects of dispersed oil to aquatic receptors. Several hundred water samples were collected for chemical analysis including PAH quantification[i]. However, not all samples for which PAHs were measured were associated with the use of dispersants. Therefore, samples with detected concentrations of one or more dispersant-related chemicals were used to screen all samples with measured PAHs concentrations. Samples with PAH composition not consistent with the source oil were not included. This screening yielded a total of 605 unique water samples. Although this criterion may have excluded chemically dispersed samples, it is impossible to distinguish natural from chemical dispersion based solely on hydrocarbon composition. Potential acute and chronic adverse effects from exposures to PAH mixtures (under the assumptions of narcosis as the mode of toxicity and PAH additively) were characterized using the Equilibrium Partitioning Benchmark Toxic Unit (TU) approach[16, ii] where values greater than one suggests that the PAH mixture may be unacceptable for the protection of aquatic organisms[16]. Using this approach, 3 and 23 of 605 samples exceeded acute and chronic benchmarks, respectively (Figure 2).

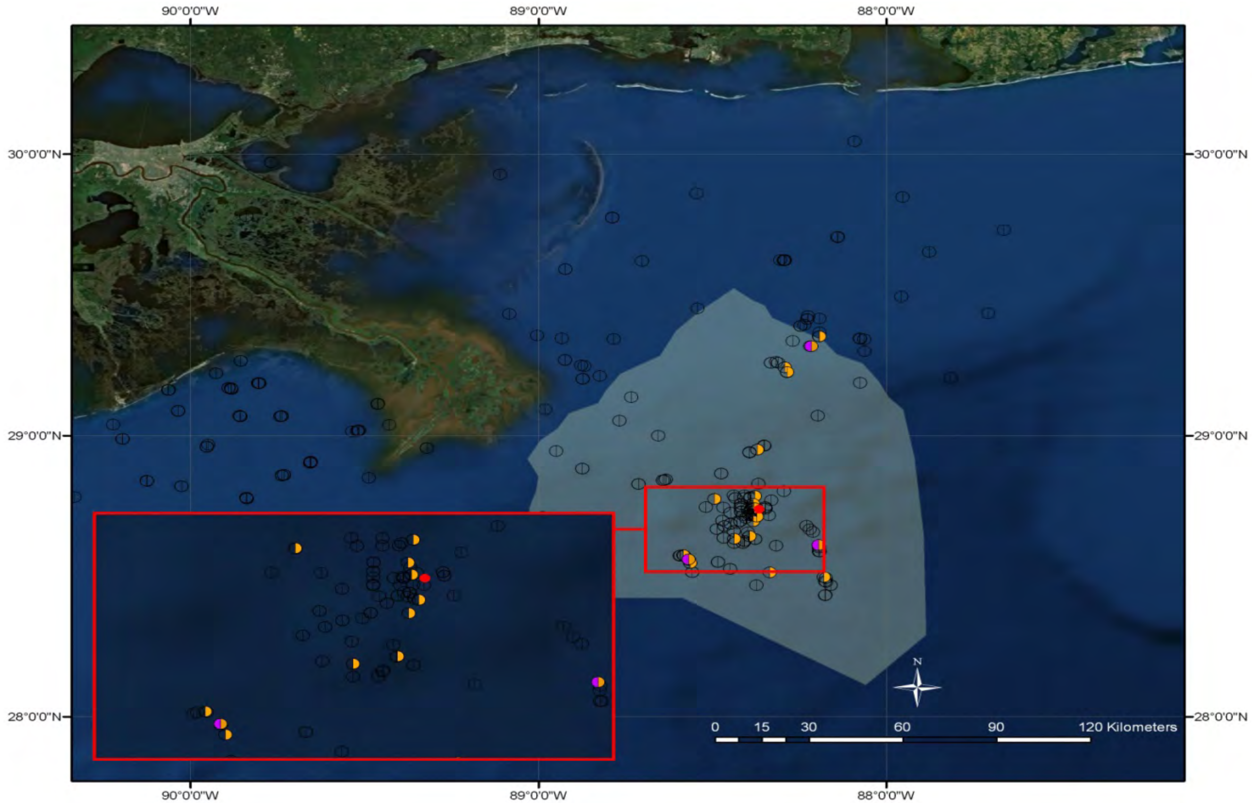

Figure 2. Acute (pink) and chronic (yellow) exceedances of PAH mixture benchmarks in samples with detected indicators of dispersants. The grey-shaded offshore-polygon depicts the area with the highest concentration of dispersant application. Red symbol approximate wellhead location.

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[i] Analytical methods included among others EPA Method 8260B, EPA Method 8260C, EPA Method 8270C SIM, EPA Method 8270C, EPA Method 8270D, EPA Method 8272

[ii] http://www.epa.gov/bpspill/water-benchmarks.html

Some of the samples identified above were collected during the SMART missions (17 May-13 July 2010)[17]. This dataset is important because the greatest risks to aquatic receptors (primarily plankton, planktonic eggs and larval fish) are from the dispersed oil in the upper portion of the water column below the dispersing oil slick. Samples collected at 1 m depth after dispersant application exceeded acute and chronic benchmarks (5 and 13 samples, respectively) consistent with a 1 to 35 fold increase in the CEWAF concentration of PAHs compared to WAF samples. Some samples collected before and after dispersant application with acute and/or chronic exceedances had detected concentrations of linear alkane analytes with low solubility and recalcitrant characteristic (i.e., phytane, pristane) suggesting the presence of non-dissolved particulate oil (oil droplets).

Of a total of ~16,000 unfiltered water samples collected concurrently with particle size analysis measurements[14], 139 exceeded acute PAH benchmarks, but most (119 samples) had detected concentrations of phytane and pristine indicative of the oil droplets. The remainder 20 samples were collected early during the response (17 May 2011) within 1 km of the wellhead. However, none of these samples had detectable concentrations of dispersant markers (propylene glycol or DPnB). An important contribution of the particle size analysis data was that most of the oil droplets (>80%) suspended in the water column (up to ~160 microns [μm]) had a diameter of <70 μm. Although it was not completely resolved whether the formation of these droplets was the result of chemical dispersion, high concentration of small particles were also observed during oil dispersion in wave tank simulations (see [14]). The formation of small particles and their slow rise through the water column (due to neutral buoyancy) are important drivers of exposure to aquatic receptors because particulate oil may have a different mode of toxicity (e.g., physical coating of body surfaces, gill uptake, ingestion; see below) than dissolved oil.

The assessments of the potential effects of dispersants and dispersed oil to benthic fauna proved difficult. Of the 775 sediment samples collected for dispersant analysis, only 8 had detected concentrations of dispersant-related compounds (only propylene glycol was detected)[11]. Only two of these samples were from offshore/deepwater areas. In light of this limited information, effects of dispersants and dispersed oil on benthic fauna represent a data gap from the DWH oil spill.

Toxicity Testing

All the toxicity testing conducted during the response focused solely on assessing acute, short-term effects and did not address chronic and declining exposures to low dispersed oil concentrations, or long-term effects. The large majority of toxicity testing was performed on water samples containing dispersants only[18, 19], or laboratory and field collected samples with chemically dispersed oil[20-23].

Toxicity from Exposures to Dispersants and Chemically Dispersed Oil

Dispersant-only tests were performed by the USEPA[18, 19] with the eight oil dispersants listed on the USEPA National Contingency Plan (NCP) Product Schedule. These aquatic toxicity tests ranked Corexit 9500A as slightly toxic to mysids, and practically non-toxic to inland silversides[18]. *In vitro* tests conducted to assess the endocrine induction potential of oil dispersants[19], found cytotoxicity at concentrations between 10 and 1000 μL/L, and no biologically significant activation of estrogenic or androgenic signaling pathways by any of the dispersants tested[19]. These tests found no indications of estrogenic activity for Corexit 9500A, and revealed generally low dispersant toxicity.

Toxicity tests performed by the USEPA showed that in all cases the dispersants alone were less toxic than the CEWAF, which in most cases had similar toxicity to Louisiana sweet crude oil WAF (Table 2). These tests also showed that oil dispersed with Corexit 9500A was moderately toxic to two standard test species[22], less toxic than oil dispersed with Dispersit SPC 1000™, and more toxic than oil dispersed with JD 2000[20]. These tests also showed the low sensitivity of the marine rotifer *Brachionus plicatilis* to MC252 oil dispersed with Corexit EC9500A compared to that of the mysid and fish test species (Table 2). Although several hundred water, pore-water, and sediment samples were collected for toxicity testing (see[23]), the response missions guiding most sample collection were not targeted for dispersants and/or chemically dispersed oils (Table 2). Some tests with samples collected during SMART (43 out of 335 tests) showed signs of toxicity, but most of these were inconclusive[21, 23]. Toxicity testing performed during subsurface dispersant application operations showed little toxicity to both *B. plicatilis* (RotoxKit M™) and the marine bacteria *Vibrio fischeri* (Microtox®)[23].

Table 2. Summary of toxicity testing with dispersants performed during Deepwater Horizon oil spill. Only currently available information was included.

Test species	Test conditions	Dispersants tested	Endpoint	Source
Juveniles (3-5 day old) mysid shrimp- *Americamysis bahia*	Continuous exposure (static, non-renewal) to CEWAF[1, 2]	Corexit® EC9500A	24 hr-LC$_{50}$: 432 µg/L 48 hr-LC$_{50}$: 186 µg/L	20
		Dispersit SPC 1000™	24 hr-LC$_{50}$: 390 µg/L 48 hr-LC$_{50}$: 198 µg/L	
		JD 2000	24 hr-LC$_{50}$: 1,298 µg/L 48 hr-LC$_{50}$: 1,012 µg/L	
Juvenile (9-14 days old) inland silverside fish- *Menidia beryllina*		Corexit® EC9500A	24 hr-LC$_{50}$: 634 µg/L 48 hr-LC$_{50}$: 571 µg/L	
		Dispersit SPC 1000™	24 hr-LC$_{50}$: 259 µg/L 48 hr-LC$_{50}$: 173 µg/L	
		JD 2000	24 hr-LC$_{50}$: 4,130 µg/L 48 hr-LC$_{50}$: 2,640 µg/L	
Newly hatched marine rotifer- *Brachionus plicatilis*		Corexit® EC9500A	24 hr-LC$_{50}$: 9,543 µg/L	
		Dispersit SPC 1000™	24 hr-LC$_{50}$: 486 µg/L	
		JD 2000	24 hr-LC$_{50}$: 5,609 µg/L	
Inland silverside fish- *M. beryllina*	Continuous exposure (static, renewal) to 100%, 50%, 10% water samples collected at 1 and 10 m depths below water surface both before and after dispersant application	Corexit® EC9500A Corexit® EC9527A	No significant mortality above controls	21
Juvenile (3-5 day old) mysid shrimp- *A. bahia*				
Marine algae- *Skeletonema costatum*			Reduced mean algal cell growth. Inconclusive results	
24-48 hours old mysid shrimp- *A. bahia*	Continuous exposure (static, non-renewal) to CEWAF and WAF[1, 3]	Corexit® EC9500A[4]	48 hr-LC$_{50}$-dispersant: 42 µg/L 48 hr-LC$_{50}$-CEWAF: 5.4 mg/L 48 hr-LC$_{50}$-WAF: 2.7 mg/L	18, 22
9-14 day old inland silverside fish- *M. beryllina*			96 hr-LC$_{50}$-dispersant: 130 µg/L 96 hr-LC$_{50}$-CEWAF: 7.6 mg/L 96 hr-LC$_{50}$-WAF: 3.5 mg/L	

[1] CEWAF = chemically enhanced, water-accommodated fraction; WAF = water accommodated fraction.

[2] CEWAF was prepared using a Dispersant-to-Oil ratio of 1:20 with fresh MC252 oil. CEWAF was analyzed using the Modified EPA Method 8270 with endpoints reported as total petroleum concentrations. [3] CEWAF and WAF were prepared following CROSERF methods[10]. CEWAF was prepared using a Dispersant-to-Oil ratio of 1:10 with fresh Louisiana sweet crude oil (lot # WP 681). CEWAF was analyzed for total petroleum hydrocarbons (TPH) following EPA SW-846, Method 8015B-DRO with endpoints reported as TPH concentrations.[4] Only showing the results for one of the eight oil dispersants. These tests followed a slight modification of the USEPA Test Method 821-R-02-012

While independent research was conducted during the response to address scientific questions regarding the effects of dispersants and chemically dispersed oils on biological receptors, it is still too early to see the results of these studies in the peer-reviewed literature. To date, one study[25] found significant reductions in the production and viability of hydrocarbon-degrading bacteria (*Acinetobacter* and *Marinobacter*) in the presence of Corexit EC9500A at concentrations of 1-10 mg/ml. However, these concentrations were several orders of magnitude above the levels in the field. Preliminary studies have also shown the uptake of dispersed oil droplets (5 μm) in an important zooplankton species in the Gulf of Mexico, demonstrating an exposure pathway to meiobenthos (Lee in [26]). Others (Wetzel in [26]) also examined coral larval mortality and settlement success (*Porites astreoides* and *Montastraea faveolata*) following exposures to spiked and declining concentrations of CEWAF from oil dispersed with Corexit 9500, and found evidences of adverse effects warranting further studies.

Toxicological testing designed to assess the effect of dissolved (e.g., filtered) vs. particulate oil (e.g., whole water) in water, to our knowledge, were not part of the response; therefore, we were unable to analyze these types of data to infer effects to aquatic receptors. Ephemeral data collection of water samples for chemical analysis that takes into account dissolved vs. particulate oil phases are part of Natural Resource Damage Assessment (NRDA) evaluations, and these datasets may become available in coming years. Other data collected as part of the NRDA process may also include samples used to evaluate acute and chronic effect of dispersants and dispersed oil.

Potential Effects at a Larger Ecological Scale

The challenges of characterizing risks from dispersants and chemically disperse oil to potential receptors are great, particularly in such a vast area impacted by the DWH oil spill. A monumental effort, undertaken in recent years, which gathered an inventory of species (from unicellular organisms to vertebrates) of the entire Gulf of Mexico, documented at least 15,419 species belonging to over 40 phyla[27]. Given such high species richness, it is virtually impossible to assess the effects of dispersants and dispersed oil to most receptors. Furthermore, for most taxa, including deepwater and benthic species, substantial gaps exist in our understanding of their spatial and temporal distributions, their basic biology (rates of growth, reproduction, and recruitment) and ecology (community structure and trophic interactions), and their sensitivity to stressors. Benthic habitats in the Gulf of Mexico (mesophotic and deep water coral reefs, other hard bottoms and soft bottoms) may be the ultimate sink of oil dispersed at the wellhead, as oil particles flocculate with suspended particles or are excreted with fecal pellets and settle out of the water column. In these habitats sessile and small species with limited mobility were likely unable to escape the cloud of chemically dispersed oil, and may have experienced long term, sub-lethal effects. These communities may have also been exposed to less weathered oil than biological communities at the surface. The poorly understood behavior of dispersed oil at depth (effects of high pressure and low temperature), and the lack of understanding on the biology of deepwater species, makes it difficult to assess short- and long-term effects. In addition, potential issues associated with the collection of soft bottom samples for toxicity testing (i.e., disruption of the surface micro layer containing dispersed oil droplets), and the lack of standard deepwater test species further complicate these assessments. Information on the long-term effects of the DWH oil spill is being assessed under subject-specific NRDA technical working groups (TWGs). Funded research projects are also underway to assess the effects of dispersants, dispersant constituents and naturally/chemically dispersed oil on Gulf of Mexico species (reef biota, deep water species, commercially important species), as well as on offshore habitats, food webs, and ecological interactions.

Effect on Planktonic Food Webs

After an oil spill, microorganisms are an important part of the degradation process but they also serve as essential members of a healthy ecosystem. Questions still remain as to how oil and dispersants affect microbial communities. Hamdan and Fulmer[28] have shown that, even at prescribed concentrations, the dispersant Corexit EC9500A is toxic to microbes involved in hydrocarbon bioremediation, but the levels of cell death from exposures differed among species. Widger *et al*[29] revealed that microbial population in water and soil samples exposed to oil and dispersant related to the DWH event showed reduced biodiversity, reduction in oxygen producing microorganisms and increased oxygen consumption by hydrocarbon metabolizing bacteria. In addition, selective degradation of hydrocarbons by different bacterial species can either increase or decrease toxic components in oil and the use of dispersant could enhance this toxicity[30]. These results indicate a species-specific tolerance of oil and dispersant and that the presence of hydrocarbons may enhance or reduce dispersant toxicity for some species of bacteria[28]. A better understanding is needed regarding the effect of oil bioremediation on microbial communities.

Although dispersed oil has been shown to negatively impact some organisms[18, 20, 22, 28, 29], satellite observations of the northeastern region of the Gulf of Mexico in August 2010 revealed increased phytoplankton biomass attributed to the DWH oil spill[31]. It should be noted that this data is based on correlation and not direct evidence due to a scarcity of field observations before and after the spill. The region in which this phytoplankton bloom occurred overlaps with the Gulf's hypoxic zone[32], leading to concerns about the impact of the oil spill and dispersant use on the Gulf's Dead Zone[33]. Bacterial decomposition of algae reduces oxygen and the presence of dispersed oil increases the abundance of hydrocarbon-degrading microbes which also consume oxygen, which could lead to further hypoxia. Dispersed oil may also be toxic to zooplankton grazers, resulting in increased algal blooms. However, dispersed oil could show toxicity to the algae itself, which may have a mitigating effect on hypoxia. Further research is required to fully understand how dispersed oil affects hypoxic systems.

Preliminary reports suggest that, shortly after the DWH incident, oil and dispersant constituents became entrained in the pelagic food web[34, 35]. Graham[35] showed that dispersed oil in the shallow water column has been incorporated into at least two trophic levels beyond prokaryotic hydrocarbon consumers. Dispersed oil has also been observed in blue crab larvae and researchers are finding potential signs of exposure extending throughout the water column based on the unusual appearance of planktonic organisms pulled up in nets (*unpub. data*)[34, 36, 37]. Contaminants from dispersed oil may result in long-term adverse effects such as carcinogenesis, impaired reproduction, shortened life-spans and decreased population numbers in planktonic organisms[34, 38, 39]. Additionally, exposure to contaminants found in oil and dispersants during early phases of the life cycle can lead to infertility and a host of developmental problems[39-41]. This is important because the area in the Gulf that was exposed to oil and dispersants included a significant portion of offshore larval and spawning grounds[27, 36]. However, exposure data from the DWH do not consistently reflect data from controlled laboratory experiments, which may not accurately reproduce field conditions or exposure regimes. The ultimate long-term effects will depend on the concentration, location and persistence of dispersed oil and the duration and timing of exposure to organisms. These factors should be further tested in ecologically relevant conditions.

Fate of the Oil and Dispersants at Depth

Subsurface Plumes

Little is known regarding dispersant behavior and oil droplet microstructure at the high pressures and low temperatures of the deep-sea. But, it has been documented that the treatment of oil with dispersant at the wellhead resulted in the formation of large, subsurface plumes made up of fine droplets of oil suspended in deep waters[42-44] (Figure 3). However, the formation of plumes is complicated due to "the interplay of gas and oil in multiphase flow, preferential solubility of each oil constituent, and potential gas hydrate formation"[42]. The effects of temperature and density gradients on oil droplet phases, changes in buoyancy during transport and transformations to the plume over time are poorly understood. It is uncertain exactly how many plumes existed and their exact fate is unknown, but they have the potential of persisting for months at depth[42, 45]. Research on plume formation and the behavior of dispersants in the deep-sea is needed to model, track and predict the fate of subsurface oil and dispersant.

Dispersed Oil Byproducts at Depth

Although the ultimate fate of petroleum hydrocarbons in deep water plumes is undetermined, Reddy *et al.*[46] demonstrated that most light-weight, water-soluble hydrocarbons (C_1-C_3) were retained in the deep water column, while insoluble fractions were deposited in sea floor sediments or transported to the surface. The retained water-soluble portions persist longer and have a much slower degradation rate than gas and n-alkane fractions[46]. Similarly, Kujawinski *et al.* [47], quantitatively revealed the sequestration of a highly water-soluble dispersant component (DOSS) at depth undergoing minimal rates of biodegradation (Figure 4). Dispersant applied at the wellhead reduced the amount of oil reaching the surface and likely increased the retention of dissolved petroleum hydrocarbons and dispersant components in the deep-sea. Additionally, MC252 oil contained lighter molecular weight hydrocarbons than typical, which would also result in increased retention of these soluble components in deep waters[34, 46]. The fate of dispersed oil byproducts in deep waters is unknown at this time; research is needed regarding their use in deep waters.

Oil and Dispersant in Deep Sediments

When interacting with suspended and deposited sediments, oil droplets form oil-sediment aggregates (OSA) and dissolved oil partitions into sediments due to capillary action and surfactant ion adsorption[48]. Model simulations demonstrate that when oil droplets and sediment particles are small (less than 0.1 mm), more OSAs are formed[48]. During DWH, the subsurface injection of dispersants facilitated the formation of small particle size oil droplets[14], potentially influencing the formation of OSAs. In addition studies have shown that due to the composition of the MC252 oil, conditions in the deep-sea and use of dispersants, more oil and dispersant remained at depth than predicted[34, 46, 48]. This has been supported with analysis of sediment samples from the sea floor which revealed the presence of oil constituents linked to MC252 oil[11, 49]. Sediments collected from within 3 km of the wellhead contained MC252 oil at levels exceeding aquatic life benchmarks, but these levels returned to reference standards within 10 km of the wellhead[11, 49]. Careful analysis of current data and further studies are required to provide a better understanding of how oil and dispersants interact with deep marine sediments.

Biodegradation

Due to the depth of the leak and difficulty in obtaining consistent samples, uncertainty and controversy surround the actual amount of microbial biodegradation of dispersed oil from the DWH spill. One study questioned the magnitude of the microbe-directed biodegradation of hydrocarbons in the plumes and concluded that the oil/dispersant plume may have persisted for months without substantial attenuation[42]. Other research has suggested that a variety of hydrocarbon-degrading microbial populations in the deep-sea responded to oil contamination by undergoing rapid dynamic adaption and that this implies an inherent bioremediation of oil contaminants in the deep-sea[50]. The research of Kessler *et al.*[51] reports that aerobic methanotrophic bacterial communities consumed a significant portion of the total hydrocarbon discharge over several months. Finally, a separate study found that the plume closest to the wellhead with the highest levels of hydrocarbons showed the least evidence of biodegradation[52]. Yet, the authors predict attenuation of the plumes over time due to highly fluctuating cycles of microbial communities influenced by persistent mixing of bacteria species, oxygen and hydrocarbons with background waters. This lack of certainty regarding the extent of biodegradation by microbes in deep-sea plumes is enhanced by the lack of knowledge regarding the effects of dispersant and dispersed oil on deep-sea bacteria. More research is required to understand the impact on oil degrading bacteria when dispersants are applied at depth.

DATA GAPS ON THE EFFECTS OF DISPERSANT USE

Prior to the DWH, many studies were done on the toxicity of dispersants (primarily Corexit 9527 and 9500) and dispersed oil ([1, 53] and references therein; [54-56]). Although studies have filled critical data gaps in the knowledge and understanding on the effects of dispersants (for example[57, 58]), the experience from the DWH clearly showed that many of the data gaps identified earlier[1, 53] still persist. In this section we build upon the NRC recommendations for additional studies based on the state of knowledge prior and after the DWH. However, an independent effort should focus on reviewing and evaluating knowledge gaps and gains from past spills (controlled or accidental) involving the use of dispersants.

General Data Gaps

Significant advances in the understanding of dispersant efficacy have been gained since the recommendations of the NRC and subsequent reports. However, all the recommendations regarding fate and effects are still relevant. Specific data gaps include: photo-enhanced toxicity; relative contribution of dissolved and particulate oil phases to toxicity; interaction of dispersed oil with sediment particles and effects to benthic fauna; tests with representative species, sensitive species and different life stages; toxicity tests that addresses delayed effects; exposures through different routes; toxicity from pathways other than narcosis (e.g., oxidative products, receptor-mediated pathways associated dissolved fractions, and smothering by oil droplets); and long-term effects on population and communities.

Comparing oil/dispersant toxicity across studies can be a challenge. Not only the preparation of WAFs and CEWAFs has differed over the years (e.g, differences in mixing energies, settling times, media treatments- filtered vs. unfiltered), but also have exposure conditions (static vs. flow-thru, closed vs. open systems, constant vs. spiked), and chemical analysis of exposure media (nominal vs. measured, particulates vs. dissolved phases, TPAH vs. TPH). Consequently, making comparative use of the existing toxicity data is almost impossible. Efforts should continue to support standardization methods and procedures (e.g., CROSERF or similar) that would allow greater comparability and reproducibility of toxicological data, and a more certain use of experimental data as scientific decision tools in future spills.

Toxicity testing under constant exposures (e.g., LC_{50} tests) does not realistically and adequately assess the risk to aquatic receptors. Under field conditions, organisms are likely exposed to multiple stressors at any given time, which could result in additive, synergistic, or antagonistic effects. But dynamic environments are expected to dilute and mix the water column, resulting in rapidly declining exposure concentrations. However, constant exposures tests may serve as conservative estimates of toxicity. The traditional constant exposure durations in standard LC_{50} (48 or 96 hours) tests should be compared to the much shorter (a few hours) and rapidly declining exposures experienced by marine organisms when oil is dispersed in open waters.

Analyses of biological effects following an oil spill have not typically focused on the effects from chronic exposures to extremely low concentrations, or have explored the potential of changes in behavioral responses (e.g., olfactory, time-response to stimuli) as indicators of exposure. These endpoints are relevant as these can lead to measurable effects at the population and community levels (e.g., increased predation; subtle changes in trophic structure and links), and should be considered in future spills.

Although chemical analyses used in spill response typically follow recommended protocols, standardization of such techniques throughout the response should be considered. Standardization of such procedures extends to the separation of dissolved vs. particulate oil phases, the use of chemical signatures, analysis of a whole suite of PAHs (beyond the 16 priority PAHs), as well as analysis of TPHs, and dispersant indicators. Efforts should also discuss acceptable method detection limits.

Data Gaps from the DWH

Temporal and spatial sampling intensity throughout the duration of the spill response should be considered when evaluating and interpreting short and long-term effects to aquatic receptors. Although several thousand samples were collected for the detection and characterization of oil constituents, sampling efforts specific to dispersants and dispersed oil were limited, and varied substantially over space and time.

The effects of low temperature and high pressures on both physically and chemically dispersed oil and dispersants are not well understood, and therefore their fate and effects in deep waters constitute a significant data gap. Although much information was gained from the DWH on the effect of dispersants on droplet size distribution at depth, future studies should focus on the correlation between oil droplet size distribution and oil constituent bioavailability and toxicity, particularly on the toxicological effects resulting from exposures to dissolved vs. particulate oil.

Another question that remains unanswered is the fate and effects of oil at depth if injection of dispersants at the wellhead had not occurred.

Most toxicity testing of dispersant and dispersed oil during the DWH response focused on 2 or 3 species, which have limited capabilities when characterizing risks to several hundred likely receptors. In addition, these tests did not sufficiently address potential differences in sensitivity to organisms living in the water-column in the Gulf of Mexico. Furthermore, the toxicity testing conducted during the response did not address the potential effects of dispersants and dispersed oil to deepwater species inhabiting areas where low temperatures can inhibit or reduce biodegradation and affect uptake and depuration kinetics. Sediment sampling of offshore deepwater bottoms was relatively limited, and so were the toxicity testing of these samples. Thus, these efforts may have not adequately quantified the impacts of subsurface injection of dispersants on these habitats, though assessments can use the state of knowledge from other spills (e.g., IXTOC, Sea Empress, Montera).

Limited *in-situ* testing was available to assess adverse effects to aquatic receptors. Rotifer toxicity tests, which are logistically simple to perform, were conducted onboard ships and used as a decision tool during subsurface application of dispersants. However, these tests are considerably less sensitive than tests performed with early life stages of fish or crustaceans. Tests species amenable to field testing aboard ship aside from rototox should be explored in the near future.

There were no studies on the photo-induced toxicity of chemically dispersed oil at the water surface. Studies should consider the increased toxicity of some PAHs in the presence of UV light by including exposures to natural sunlight or ultraviolet light. Also, most of the toxicity assessments conducted during the response were confined to PAHs (either total PAHs or comparisons versus benchmarks), and did not take into account other oil-related constituents (e.g., diesel range organics, normal alkanes, isoparaffins, heterocycles and unresolved complex mixtures) which may also contribute to the overall toxicity of dispersed oils.

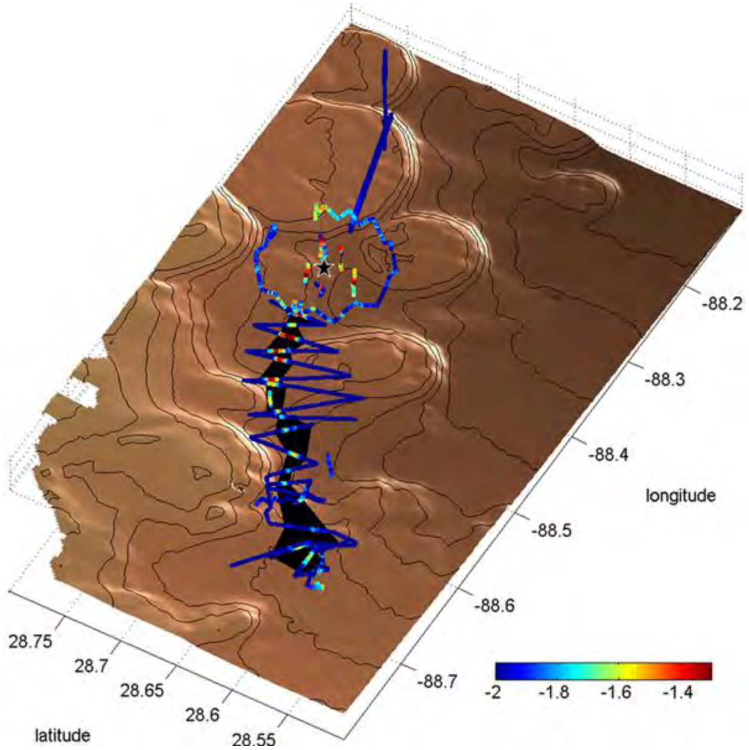

Figure 3. A 35 km long oil plume at ~1000-1200 m depth near the DWH wellhead (indicated by black star) discovered using mass spectrometry and fluorescence data to detect monoaromatic petroleum hydrocarbon concentrations (from[42]).

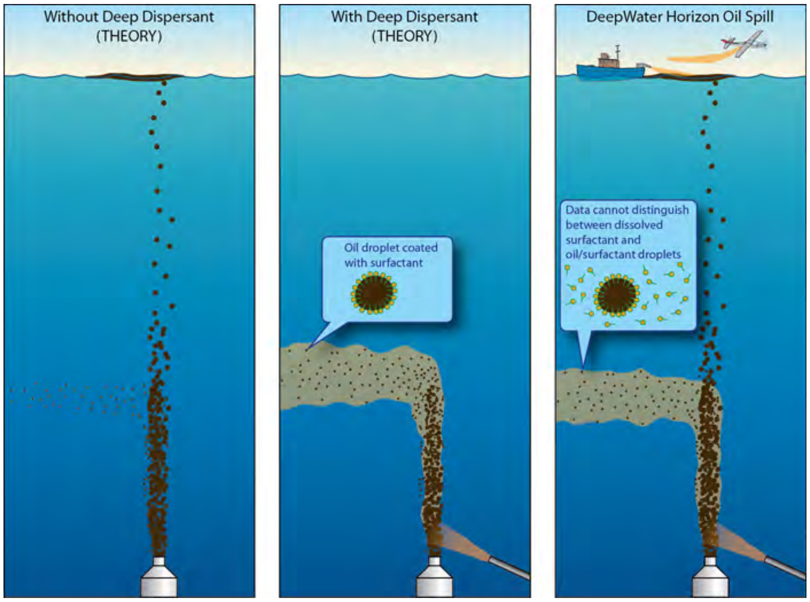

Figure 4. Ultrahigh resolution mass spectrometry and liquid chromatography were used to identify and quantify the surfactant DOSS in deepwater during and after DWH oil flow. The first two panels show the general theories of the fate of oil with and without dispersant application at the wellhead. The third panel suggests that dispersant remained in the deep waters plume, associated with oil and gas phases, and that dissolved surfactant could not be distinguished from surfactant coating oil droplets (from[47]).

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Dispersants and Seafood Safety
Assessment of the potential impact of COREXIT® oil dispersants on seafood safety

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The April 20, 2010 explosion and subsequent sinking of the Deepwater Horizon oil production platform (DWH) resulted in the largest oil spill in U.S. history. On April 29th, a Spill of National Significance was declared as roughly 53 thousand barrels of oil per day flowed into the Gulf of Mexico (GOM). The U.S. Coast Guard estimated 4.9 million barrels of crude oil escaped before the damaged DWH wellhead was sealed on July 15, 2010 (National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling 2010). Oil spill clean-up methods included skimming operations, burning of surface oil, siphoning oil into tankers directly from the wellhead, and the application of chemical dispersants. The first 3 methods mentioned above physically removed spilled oil from GOM waters. The last method, chemical dispersion, distributed insoluble fractions of the oil into the water-column. This was done for 3 reasons: 1) to reduce the exposure of response personnel at-sea to volatile organic compounds emanating from the surface slick; 2) to prevent concentrated surface oil from reaching, and damaging, fragile coastal wetlands, beaches and shoreline ecosystems; and 3) to accelerate the break-down of spilled oil by natural microorganisms in the environment. During oil spill response, the Regional Contingency Plan (RCP) applicable to the GOM (EPA Regions 4 and 6 within the National Response Framework) pre-authorized the use of Nalco Co. (Naperville, IL) oil dispersants Corexit® 9527 and Corexit® 9500 among other pre-approved product formulations. From April 22 to July 19, 2010, an estimated 1.1 million gallons of Corexit® dispersant were applied over approximately 300 square miles of oiled surface waters in the GOM and 771,000 gallons were injected directly into the oil free-flowing from the wellhead 5,100 feet beneath the surface (National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling 2010). Corexit® 9527 comprised approximately 215,000 gallons (~11%) of the total dispersant volume applied to the surface oil slick and was discontinued on May 22. The unprecedented volume of chemical dispersants used to combat the DWH oil spill elicited public concerns for the health of responders, coastal communities, marine life, and the safety of seafood from impacted areas of the GOM. This document will address the latter of these concerns.

As part of the federal response to the DWH oil spill, the FDA and NOAA assessed Corexit® dispersant ingredients for toxicity and potential to bioconcentrate in seafood species. With the exception of one proprietary component, the chemical compositions of Corexit® 9527 and Corexit® 9500 were identified in material safety data submitted to EPA as required by subpart J of the National Contingency Plan (NCP), Sec. 300.915 for RCP pre-authorization (EPA 2010a; 40 CFR 300.915). As it became apparent that large volumes of dispersants were being used to combat the subsurface and surface oil spill, EPA requested and received from the manufacturer disclosure of the proprietary component (i.e. dioctyl sodium sulfosuccinate, DOSS). Corexit® constituents are listed in Table 1 and described below.

Table 1. From http://www.epa.gov/bpspill/dispersants-qanda.html#list

CASRN	Name	Corexit® 9527	Corexit® 9500
111-76-2	2-Butoxyethanol (ethylene glycol mono-n-butyl ether)	X	n/a
57-55-6	Propylene glycol	X	X
29911-28-2	Dipropylene glycol monobutyl ether	X	X
577-11-7	Dioctyl sodium sulfosuccinate	X	X
64742-47-8	Petroleum distillates, hydrotreated light fraction	n/a	X
1338-43-8	Sorbitan, mono-(9Z)-9-octadecenoate	X	X
9005-65-6	Polyoxy-1,2-ethanediyl derivatives of sorbitan, mono-(9Z)-9-octadecenoate	X	X
9005-70-3	Polyoxy-1,2-ethanediyl derivatives of sorbitan, tri-(9Z)-9-octadecenoate	X	X

The solvent 2-butoxyethanol (CASRN 111-76-2) is a high production glycol ether and constituent of Corexit® 9527. It has other common uses as a solvent and degreaser in industrial, residential, and personal care products including protective surface coatings (spray lacquers and paints), agricultural chemicals, household cleaners, and liquid soaps and cosmetics at concentrations of up to 10%. This compound is approved by FDA as an indirect and direct food additive for use as an antimicrobial agent, defoamer, stabilizer and component of adhesives (21 CFR 175.105(FAP 1B0233); 178.1010(FAP 4A1375); 176.210(FAP 3B0899); 177.1650; 173.315(FAP 5A3079). FDA approval means that the compound is safe for its approved intended uses and the human exposures associated with those uses. 2-butoxyethanol has been well studied. Information is available on metabolism, mechanism of toxicity, pharmacokinetics and impact of exposure on human health. Primary effects are on the hematologic system with secondary renal effects. Acute oral LD_{50} values in a variety of rodent animal models range from 200 to 12,750 mg/kg bw. The Agency for Toxic Substances and Disease Registry (ATSDR, 1998) derived minimal risk levels (MRL[1]) of 0.4 mg/kg bw d^{-1} for human acute-duration (14 d) and 0.07 mg/kg bw d^{-1} for human intermediate-duration (15-364 d) oral exposures. Acute oral exposures of humans to large amounts of 2-butoxyethanol have been shown to cause coma and respiratory depression in addition to hematotoxic effects, although this route of exposure is the least likely for the general population. From quantitative structure-activity relationships, the bioconcentration

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[1] An MRL is defined as an estimate of daily human exposure to a substance that is likely to be without an appreciable risk of adverse effects (noncarcinogenic) over a specified duration of exposure. MRLs are derived when reliable and sufficient data exist to identify target organs(s) of effect or the most sensitive health effects(s) for a specific duration within a given route of exposure. MRLs are based on noncancer health effects only and do not reflect a consideration of carcinogenic effects. MRLs can be derived for acute, intermediate, and chronic duration exposures for inhalation and oral routes.

factor (BCF) for 2-butoxyethanol has been predicted to be 3, and experimentally estimated in fathead minnows (*Pimephales promelas*) to be 2 (ASTER 1995). The physical-chemical characteristics of 2-butoxyethanol include vapor pressure of 0.88 mm Hg at 25^{o}C (ATSDR 1998), Henry's law constant estimates ranging from 2.08 x 10^{-8} to 3.61 x 10^{-6} atm- m^3/mol at 25^{o}C (HSDB 1995, ASTER 1995), and log octanol-water partition coefficient (log K_{ow}) of 0.83 suggesting a low probability of lipid uptake or bioconcentration in fish (ATSDR, 1998*)*. The half-life of 2-butoxyethanol in surface waters is estimated to be in the range of 7-28 days, and the chemical is reported to be readily biodegraded in aerobic soil and aquatic environments (Howard et al., 1991, HSDB 2010).

Propylene glycol (CASRN 57-55-6) and dipropylene glycol monobutyl ether (CASRN 29911-28-2) are constituents of both Corexit® 9527 and 9500. Dipropylene glycol monobutyl ether is used as a solvent for industrial and residential cleaners/degreasers, paints and plasticizers. Propylene glycol is used in commercial formulations of foods, drugs, cosmetics, and personal care products (e.g. toothpaste, shampoo, mouthwash). Propylene glycol is approved by FDA as a Generally Recognized As Safe (GRAS) ingredient, direct food additive, and indirect food additive for many uses, including as an anticaking agent, antimicrobial agent, antioxidant, color or color adjunct, defoamer, dough strengthener, emulsifier, flavoring agent, formulation aid, humectant, processing aid, solvent, diluent or vehicle stabilizer, thickener or gelling agent, surfactant, and texturizer (21 CFR 175.105(FAP 1B0233, FAP 2B0650); 178.3300; 175.300; 175.320; 177.2420; 177.1680(FAP 5B1808); 184.1666). Propylene glycol ethers as a class are rapidly absorbed and exhibit low acute toxicity by oral exposure and **propylene glycol is infrequently associated with adverse effects.** Acute oral LD_{50} values in a variety of rodent animal models range from 3,000 to 5,000 mg/kg bw for dipropylene glycol monobutyl ether and from18,000 to 46,000 mg/kg bw for propylene glycol (OECD 2003, HSDB 2010). Some acute oral data exist for humans, but the information is limited and includes systemic and neurological effects at high levels of exposure. No MRL for oral exposure to propylene glycol in humans has been derived because data are insufficient (ATSDR, 1997). The FAO/WHO Joint Expert Committee on Food Additives (JECFA) determined 25 mg/kg bw d^{-1} as the acceptable daily intake (ADI) for propylene glycol (FAO/WHO, 1997). Predicted BCFs for dipropylene glycol monobutyl ether and propylene glycol are <10 indicating a low potential for bioconcentration in aquatic food chains (OECD 2003, HSDB 2010). Physical-chemical characteristics include vapor pressures below 1 mm Hg, Henry's law constants ranging from 1.2 – 1.7 x 10^{-8} atm m^3/mol at 25^{o}C, and log K_{ow} from -0.92 to 1.52 suggesting low probability of uptake in lipids or bioconcentration in fish. Propylene glycol and glycol ethers would be expected to be of low to moderate volatility from water and readily biodegradable in aquatic and terrestrial environments with half-lives of 7-28 days (Howard et al., 1991; ATSDR 1997; Staples and Davis 2002; OECD 2003; HSDB 2010).

Petroleum distillates, hydrotreated light fraction (CASRN 64742-47-8) are paraffinic dearomatized, and volatile solvents derived from crude petroleum, and constituents of Corexit® 9500. Production quality of light petroleum distillates is highly variable and common uses include as a solvent for paints, varnishes, polishes, and lubricants, and general purpose cleaners and degreasers. Hydrotreated light petroleum distillates Norpar 13 (food grade aliphatic n-alkanes ranging from nonane to hexadecane: CASRN 94094-93-

6) were reportedly substituted for 2-butoxyethanol in the formulation of Corexit 9500 (NRC 2005); however, CASRN do not align with that reported by EPA (Table 1). FDA has approved similar food grade odorless light petroleum hydrocarbons as indirect and direct food additives (21 CFR 172.884; 175.105; 176.200; 176.210; 178.3650). C_8 – C_{20} range aliphatic hydrocarbons comprising petroleum distillates, hydrotreated light fraction exhibit low acute oral toxicity. Acute oral LD_{50} values in rodent animal models are greater than 5,000 mg/kg (HSDB 2010). Subchronic toxicity studies suggest the aliphatic hydrocarbon fluids to be relatively non-toxic (EPA 2006). Predicted BCFs range from 60 to 80 and physical-chemical characteristics include vapor pressures below 2.0 mm Hg; Henry's law constant ranging from 0.2 – 3.4 atm-cu m^3/mol, and log K_{ow} from 2.2 to 5.4. Some of the longer chain compounds in the mixture may have a high potential for concentration in aquatic organisms provided they are not volatilized or metabolized. Petroleum distillates are volatile from water and readily biodegradable in days to weeks (EPA 2006, HSDB 2010).

Dioctyl sodium sulfosuccinate (DOSS; CASRN 577-11-7) is an anionic surfactant (butanedioic acid, 2-sulfo-1,4-bis(2-ethylhexyl) ester, sodium salt) listed as a proprietary organic sulfonic acid salt constituent of both Corexit® 9527 and 9500 formulations. Other common uses include wetting and flavoring agent in food, industrial, and cosmetic applications, and a medicinal stool softener in over-the-counter use. FDA has approved this compound as a GRAS ingredient, and as indirect and direct food additives under prescribed conditions of use (21 CFR 73.1; 131.130; 133.124; 133.133; 133.134; 133.162; 133.178; 133.179; 163.117; 168.115; 172.520; 172.808; 172.810; 175.105). DOSS was determined to be essentially non-toxic by oral administration to rodent animal models with acute toxicity ranging from 2.6 to 5.7 g/kg bw. Diarrhea and signs of intestinal irritation were noted. Three-generation reproduction studies in rodent models did not reveal adverse effects; however, parental and weanling weight loss was noted at dose levels above 5 g/kg bw (FAO/WHO 1991a). JECFA determined 0.1 mg/kg bw d^{-1} as the ADI for dioctyl sodium sulfosuccinate (FAO/WHO 1995). Predicted and experimentally derived BCFs are <10, indicating a low potential for bioconcentration and bioaccumulation (Goodrich et al., 1991). Physicochemical characteristics include vapor pressure of 2.17×10^{-11} mm Hg, Henry's law constant 5×10^{-12} atm m^3/mol, and log K_{ow} 6.1. DOSS is essentially nonvolatile from water and several studies have reported >90% biodegradation in 3-12 days at freshwater concentrations of 3.3-12.9 ppm (HSDB 2010).

The nonionic surfactant Span 80 (CASRN 1338-43-8) is a trade name for sorbitan, mono-(9Z)-9-octadecenoate. The nonionic surfactant Tween 80 (CASRN 9005-65-6) is a trade name for a mixture of isomers and congeners of polyoxy-1,2-ethanediyl derivatives of sorbitan, mono-(9Z)-9-octadecenoate. The nonionic surfactant Tween 85 (CASRN 9005-70-3) is a trade name for a mixture of isomers and congeners of polyoxy-1,2-ethanediyl derivatives of sorbitan, tri-(9Z)-9-octadecenoate. Numerous chemical synonyms and trade names exist for these materials. Other common uses for Span and Tween products include as wetting agents, solubilizing agents, or emulsifying agents in cosmetic and personal care products. Span 80 and Tween formulations are widely used in food products, cosmetic and personal care products, oral pharmaceuticals, and parenteral products. They include GRAS direct and indirect food additives commonly known as polysorbates (21 CFR 73.1;

107.105; 172.515; 172.623; 172.836; 172.838; 172.840; 172.842; 173.310; 173.340; 175.105; 178.340). The National Toxicology Program reviewed Tween 80 (CASRN 9005-65-6) for developmental toxicity in rats and estimated a maternal LOAEL of 500 mg/kg-day based upon an increase in maternal liver weight at this dose. No definitive adverse effects on prenatal development were noted and the developmental NOAEL was projected to be greater than 5,000 mg/kg/day (NTP 1992). JECFA determined 25 mg/kg bw d^{-1} as the ADI for Tween 80 and Span 80 (FAO/WHO, 1973). Predicted BCF/BAF for sorbitan oleates have been estimated from 36 to >300 suggesting potential for bioaccumulation. Physical-chemical characteristics of the sorbitan oleates include vapor pressures less than1 x 10^{-10} mm Hg at 25^{o}C; Henry's law constants <1 x 10^{-10}; and Log K_{ow} from <1 to 6 (KOWWIN v1.54; v1.67; HENRYWIN v3.20; Rorije et al., 1997; EPA 2010c). Sorbitan oleates would not be expected to volatilize from water and are readily biodegradable (HSDB 2010).

The aquatic toxicity of dispersant formulations has been examined and debated over many years. Following extensive reviews in 1989 and 2005, and suggested standardization of testing methods, dispersants in use today are generally reported to be less toxic than formulations prior to 1970 (e.g. NRC 1989, 2005, Fingas 2008). Corexit® dispersants in particular have been well studied with most reports indicating lower aquatic toxicity in direct comparisons with water soluble, water accomodated and chemically dispersed oil fractions (e.g., George-Ares and Clark, 2000; Liu et al., 2006; Judson et al., 2010; Hemmer et al., 2011). Other studies have addressed dispersant influence on the bioavailability and uptake of aromatic and aliphatic constituents of oil by various aquatic species (e.g. Milinkovitch et al., 2011; Jung et al. 2009; Mielbrecht et al., 2005; Fuller et al., 2004; Ramachandran et al., 2004; Cohen et al. 2001; Gagnon et al. 2000; Singer et al., 1998). However, the potential for dispersant constituents themselves to accumulate in aquatic species has received less attention. Several studies investigating uptake and disposition of principal dispersant constituents, ionic and nonionic surfactants, in aquatic species suggest rapid uptake, metabolic conjugation, concentration in liver and bile with transient enterohepatic circulation, and rapid elimination (Alvarez-Munoz et al., 2010; Tolls et al., 2000; Tolls & Sijm 1999; Goodrich et al., 1991; Granmo & Kollberg 1976; Calamari & Marchetti 1973). Distribution of surfactants into muscle tissues was reported to be low order and low BCF values for edible tissues. In one of few studies to assess the uptake and disposition of Corexit® constituent dioctyl sodium sulfosuccinate in aquatic species, Goodrich et al. (1991) noted rapid uptake and concentration in viscera and bile of rainbow trout, at significantly higher levels than uptake in either blood and carcass. BCFs were not determined for viscera or bile due to the lack of steady state conditions. BCFs of 3.47 and 3.78 were derived for blood and carcass compartments, respectively, indicating little bioconcentration in edible tissues.

The initial federal chemical safety assessment of Corexit® dispersants in the context of seafood safety included structure-activity modeling to estimate BCFs for Corexit® constituents. Consistent with existing information, predictive BCFs for Corexit® constituents, other than the nonionic surfactants and light petroleum distillates, fell below 10, suggesting low potentials for bioconcentration and accumulation in edible tissues of aquatic species. The BCFs for light petroleum distillate mixtures ranged from 60 to 80.

Nonionic surfactant BCFs have been experimentally determined in fathead minnow with an average value of 39.6 and maximum value of 387, suggesting moderate potential for bioconcentration. However, high elimination rate constants indicated that these compounds are rapidly biotransformed *in vivo* are thus unlikely to accumulate in fish (Tolls et al., 2000). Dispersant concentrations in DWH surface applications at sea were estimated by the manufacturer to be approximately 30 µg/L in the area of the oil slick to a depth of 10 meters (Nalco, 2010). Previous research (Georges-Ares & Clark, 2000; NRC 1989) indicates that dispersant would be expected to be rapidly diluted and biodegraded in the ocean environment to levels below detection. Analyses for Corexit® constituents in surface water and sediment samples from the GOM after dispersant applications had ceased did not detect dispersant chemicals above limits of detection (EPA 2010b). However, deep subsurface sampling and analyses detected trace levels (12 ppb) of DOSS entrained in a hydrocarbon plume at 1000-1200 m water depth, suggesting slow to negligible degradation at depth (Kujawinski et al., 2011).

In the development of a method for surveillance of dispersant residues in GOM seafood species, the FDA and NOAA performed controlled exposures of Corexit® 9500 to live Eastern oyster (*Crassostrea virginica*), blue crab (*Callinectes sapidus*), and red snapper (*Lutjanus campechanus*) to generate incurred residues (Benner et al., 2010). DOSS was selected as the indicator compound for potential Corexit® contamination in seafood due to its inclusion in both Corexit® formulations, extremely low volatility, and potential to persist in the environment. The laboratory exposure studies were designed to generate incurred residues in seafood species to support method development and validation under a compressed time schedule, and therefore procedural design was not intended to be sufficient for rigorous pharmacokinetic assessment and environmental relevance. Nevertheless, it was possible to incorporate a limited sampling of uptake and depuration time points in the species exposed.

Performance testing of a rapid extraction procedure and liquid chromatography tandem mass spectrometry (LC-MS/MS) method for DOSS showed an average recovery of 92% and relative standard deviation of 11%. The method limits of detection (LOD) for DOSS in seafood species ranged from 0.003 µg/g (FDA Forensic Chemistry Center) to 0.015 µg/g (NOAA Northwest Fisheries Science Center) and limits of quantitation (LOQ) from 0.010 µg/g to 0.045 µg/g (Flurer et al., 2011). Mean DOSS concentrations in laboratory exposed and depurated oysters exposed to 100 mg/L Corexit® 9500 were 18 and 12 µg/g after 24 and 48 h of exposure, respectively. Levels of DOSS declined by >99%, to 0.023 µg/g within 72 h of depuration in clean water. In crabs exposed to Corexit® 9500 (100 mg/L) for 24 h, mean DOSS level in muscle was 0.9 µg/g, with levels declining to 0.023 µg/g (>97%) within 72 h of depuration in clean water. After 24 h of exposure, mean DOSS concentration in crab hepatopancreas was 11 µg/g, more than 10-fold higher than corresponding muscle tissue. Levels increased initially during the first 24 h of depuration, possibly as a result of the re-distribution of residues within the body during elimination. Levels subsequently declined >95% to 2.4 µg/g after 72 h of depuration. DOSS concentrations in muscle tissues of red snapper exposed to 100 mg/L Corexit® 9500 for 24 h were near or below the LOQ at all sampling times (Benner et al., 2010).

In retrospective analyses of 393 GOM fisheries re-opening samples collected from June 2010 through March 2011, DOSS was not detected in 116 of 119 samples collected from State waters. Three samples from State waters showed DOSS levels ranging from 0.011 to 0.013 µg/g (FDA 2010a). Of 274 samples analyzed from Federal waters, 12 finfish samples contained DOSS ranging from 0.037 to 0.41 µg/g. Overall, DOSS was detected at or above the LOQ in less than 3.6% (14/393) of the re-opening samples tested and all were below safety thresholds determined for DOSS in finfish (100 µg/g), shrimp and crabs (500 µg/g), and oysters (500 µg/g). Safety thresholds were derived by combining the 2005-2006 National Health and Nutrition Examination Survey (NHANES) 90th percentile finfish, shrimp or crab meal size adjusted by the 90th percentile consumption frequency with the acceptable daily intake for DOSS developed by the World Health Organization, Food and Agriculture Organization, Joint Expert Committee for Food Additives (FAO/WHO 1991a, 1995, FDA 2010b).

Conclusions:

In considering the potential for chemical dispersants to compromise the safety of GOM seafood, initial questions concerned the potential toxicity of dispersant constituents, their concentrations, fate and persistence in the environment, their potential for bioconcentration in seafood species, and their disposition and persistence in seafood species. With the exception of dipropylene glycol monobutyl ether, the constituents of Corexit® dispersants are recognized direct or indirect food additives under prescribed conditions of use. Corexit® dispersants used to treat the DWH oil spill were rapidly and extensively diluted in GOM waters, and environmental concentrations, estimated and measured, were commensurately low when detected. The physical-chemical characteristics and scientific literature indicate that dispersant constituents are susceptible to chemical and biological degradation, and that the potential for bioconcentration and persistence in the edible tissues of seafood species is low. The modeling, experimental, and field assessments performed during the response to the DWH oil spill, as well as the knowledge base accessed through scientific literature, indicated that Corexit® dispersants did not pose a threat to the safety of GOM seafood during or after their use. However, oil spills in different parts of the world differ in the nature and extent of public and environmental health hazards entailed, and consequently response strategies are rarely the same. There are numerous dispersant formulations available to responders, and in development for mitigation of oil spills under varying conditions. Future responders would benefit from a systematic assessment of all dispersant constituents, and their fate in aquatic species. A review of the existing knowledge base for dispersant constituents that are listed on the NCP product schedule should be performed to determine chemical makeup, environmental fate, kinetics, BCF/BAF, and potential human toxicity through direct or indirect exposure in order to identify constituents of potential public health concern. Some level of standardization of experimental designs informed by the needs of risk analysis, and testing methods for toxicologically valid markers of dispersant contamination in aquatic species would benefit risk managers and responders in the event of future oil spills.

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Dispersants and Risk Communication

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Dispersants and Risk Communication

Background

Risk communications is a research area of the social sciences which is closely associated with human dimensions and external communications. External communications, traditionally in the purview of public affairs, may have multiple purposes including influencing public beliefs, opinions, and judgments about the incident. Risk communications on the other hand:

- Includes actions, words, and other interactions that incorporate and respect the perceptions of the information recipients, intended to help people make more informed decisions about threats to their health and safety (Ropeik, 2008).
- Ropeik, D. 2008. Risk Communication: More Than Facts and Feelings. International Atomic Energy Commission Bulletin. 50-1:58-60.
- Is the interactive process of exchange of information and opinions among individuals, groups, and institutions concerning a risk or potential risk to human health or the environment. (National Research Council, 1989)National Research Council, Committee on Risk Perception and Communication. Improving Risk Communication. National Academy Press, Washington, DC. 1989.
- Means communication intended to supply lay people with the information they need to make informed, independent judgments about risks to health, safety and the environment. (Morgan et al 2001) Morgan, M.G., B. Fishoff, A. Bostrom and C.J. Atman. 2001. Risk Communication: A Mental Models Approach. Cambridge: Cambridge University Press.

There are many approaches toward risk communications. Some of them focus on improving the way external communications about risks are conducted, e.g., developing better messages, and some focus on the content of risk communications, that is, sharing technical information to support the assessment of the potential for risks. Better messages, engagement, and risk-based communications were needed during DWH.

Dispersants as an oil spill response tool have been studied for effectiveness and effects for over 40 years. Numerous studies conducted by academia, industry, and government agencies have provided important scientific information on dispersants and their effects on oil and the environment (Rowe et al., 2009; Khelifa et al., 2008; Lee, 2004). The general findings have been that dispersants have become less toxic and more effective since their original formulations. It is a generally accepted guideline that if the dispersant is compatible with the specific oil and there is sufficient water depth (10 meters or greater) and environmental conditions (water temperature and wave height) are right, dispersants may have a positive effect on reducing shoreline oiling and increasing the biodegradation rate of the oil. The specific environmental trade-off analysis for any given situation needs to be weighed and appropriate actions taken. To provide some background, the extended quote below from a 1993 EPA document (Use of Chemical Dispersants for Marine Oil Spills), reveals the fact that practical considerations for dispersant use have historically been complex and contentious:

> During an oil spill, a confluence of competing interests must be balanced. The news media likely will be on the scene requesting statements on any action that is being taken to respond to a spill event. Various interested parties such as representatives of the vessel owner, the cargo owner, local fishing interests, businesses dependant on tourism, local/state/federal government agencies, environmental organizations, equipment vendors, and cleanup companies will appear on the scene and advocate their position to both the OSC and the press. Often the various groups approach spill response from a different base with different objectives. Decision making, management, and organization of a spill response are made more difficult by maintaining open communication with the various interest groups; but eventually the effort to maintain the interaction and develop it organizationally can result in a much more effective response. Management and organization of oil spill responses have been studied (Cohn et al, 1991; Noble, 1991), but there are no tested paradigms that account for the rapid action and public input required in a crisis situation.
>
> With the multitude of problems that can arise in the U.S. legal environment and the strong antipathy toward the use of dispersants that has developed among some interested parties, the OSC should reflect carefully on dispersant use and be ready for criticism. Two considerations guide the decision-making process affecting an actual dispersant use situation:
>
> - There is a reasonable probability of measureable success (e.g., preventing oil from reaching a beach or breeding area).
>
> - Consensus agreement has been reached between potentially affected parties that dispersant application is worthy of being evaluated as a response.
>
> Measureable success, even if it is not complete, will vindicate the decision to use a dispersant. Although it may not be required, a consensus agreement will help to defuse critics who challenge a response that does not achieve success. Numerous other considerations will come into play in a response involving the prospect or the actual use of dispersants. It is beyond the scope of this document to attempt to identify all of the possibilities. The final decision will be based on the experience,

> understanding, and knowledge of the decision makers and their risk tolerance.

At the Deep Water Horizon (DWH) response there was some degree of measurable success, however, the consensus agreement in place prior to the spill was superseded by the magnitude of the spill and subsequent large amount of dispersants applied. The breakdown of consensus among government agencies contributed to public concern regarding the use of dispersants. For example, the state of Louisiana abstained in its vote for use of dispersants and the EPA began requiring additional topological testing and limitations on dispersants.

Consensus Environmental Risk Analysis

Since the late 1990s, through the Consensus Environmental Risk Analysis (CERA) process (Aurand, 1999), NOAA, the US Coast Guard and various stakeholders have worked with several USCG Sectors and Area Committees to evaluate various oil spill response options, identify specific biological resources at risk, seasonality, and through scenario-based gaming weigh the relative pros and cons of different response actions. The CERA approach was derived from EPA's Ecological Risk Assessment framework and guidelines (US EPA). These CERAs have involved local, state, and federal agencies that would participate in the decision-making process, as well as natural resource scientists and other stakeholders, e.g., NGOs and fisher representatives when available. This model has proved to be a valid and methodical way to assess and discuss trade-offs before an actual spill event.

A meeting convened by the CRRC entitled "Deepwater Horizon Dispersant Use Meeting," was attended by over 50 scientists, engineers and spill response practitioners from numerous organizations, including: U.S. Coast Guard (USCG), Mineral Management Service (MMS), National Oceanic and Atmosphere Administration (NOAA), industry, state government, and academia. The ultimate goals of this meeting were to: (1) Provide input to the affected Regional Response Teams (RRTs) on the use of dispersants going forward in the DWH incident; and (2) Identify possible new monitoring protocols in the event of continuing aerial and subsurface dispersant application (Coastal Response Research Center. 2010.)

Two of the conclusions from this report that are germane to this topic are:

> It was the consensus of this group that up to the time of the meeting, use of dispersants and the effects of dispersing oil into the water column had generally been less environmentally harmful than allowing the oil to migrate on the surface into the sensitive wetlands and near shore coastal habitats.
>
> For the DWH spill, the RRTs should provide for a continual re-evaluation of tradeoff options going forward. Because of the magnitude of the DWH spill and with the expectation of prolonged dispersant application, the RRTs should consider commissioning a Consensus Ecological Risk Assessment, or equivalent,

including use of existing temporal and spatial data on the resources at risk and using the most current environmental data.

These recommendations were not performed. Had they been enacted some additional degree of confidence regarding the use of dispersants may have been achieved for the general public.

The response to the DWH spill had limited success with regard to communications between various agencies, BP and the Coast Guard that reflected the CERA process. The need to develop specific risk communications for dispersants was raised by the Coast Guard in Houma, LA in late May, but by then the negative public perception regarding dispersants was well underway. Effective risk communication is a complex process where information and opinions are shared by risk management institutions with an involved public. Risk communication attempts to build consensus concerning accurate information through open and informed discourse (Fischoff et al. 1981).

Beginning in early June, Unified Command initiated community meetings in Louisiana provided an important opportunity for stakeholder engagement and dialogue. These meetings informed the development of risk communications and respond to stakeholder questions and concerns. Also, BP began developing risk communication messages from the JIC with input from dispersant and other technical specialists. However, risk communications as a specific function was new to the incident command system process and perceived primarily as targeted messaging. In this regard, there was no consensus agreement for public involvement and how to apply risk communication principles in communicating issues of risk and safety to the public.

What has not been as well studied is the way to convey this decision-making to the general public. There have been several studies conducted on spill risk communications (Tuler, et al. 2008; Tuler and Webler. 2008; Scholz, et al.1999). However, this line of research provides little information on how the decisions were made (ICS process), potential human impacts (low), fate of the oil (biodegradation), trade-offs (shoreline and surface vs. water column impacts), what dispersant are made of (formulations and other everyday products they are found in), etc. Most likely, this was due to the much smaller amounts used in the past and the very short time duration during which they were applied. Prior to DWH, agencies who made pre-authorization and incident-specific decisions about the use of dispersants apparently envisioned spills that resulted from vessels or pipelines, i.e., involving a release of oil over a short duration, e.g., on the order of hours to a few days. Blowouts had occurred in the past and therefore were within the US dispersant experience; nevertheless, no pre-authorization agreements contain explicit restriction of dispersants to a limited duration. Indeed, contingency plans have focused on “ecological issues” and human dimensions, e.g., economic, sociological and cultural risks, have received very limited attention (Webler and Lord. 2010). Given that a rather substantial body of research on the Exxon Valdez oil spill reveals severe and chronic impacts to human populations, more direct concern needs to focus on human dimensions (Picou et al. 2009; Picou. 2009). In particular, strategic risk communications regarding the use of dispersants and their consequences for the ecology and human health should be addressed.

DWH Outreach Efforts

There were multiple efforts to inform the public about the necessity to use dispersants during the response to the DWH spill. The Public Affairs and Liaison Units in conjunction with the Environmental Unit (EU) prepared numerous press releases, public information brochures, posters, talking points, graphics, and statements. The objective of these activities were to inform the media and general public on the reasons dispersants were being used, the rationale behind the decisions, the efforts to monitor the applications, and the successes that were achieved.

From the vantage point of the command post, it appeared that the messages were being received in the fashion that they were intended. Early in the incident several people came from Alaska to talk with the fishing communities about their experiences during the *Exxon Valdez* spill, in the interest of helping Gulf communities prepare for what to expect. An important assumption was made prematurely that the two spills, and therefore the effects, were very similar and that the Gulf experience would closely parallel the Alaska experience. Some significant differences in the two spills were not acknowledged (e.g., locale, environment, oil, etc.). As a result of these interactions, some people in the community, including fishermen, developed negative sentiments toward dispersant applications or the addition of “chemicals.” The Alaskan visitors to the Gulf spoke of people getting ill and fish dying. The Unified Command staff in the command post was not pro-active enough to get ahead of the negative stories being promulgated. The media took the sensationalism of the 20-year-old Exxon Valdez saga and retold them to larger audiences. Many examples of the ecological and social consequences of the *Exxon Valdez* spill were supported by peer reviewed journal articles and research funded by recognized agencies such as the National Science Foundation (Rice. 2009; Picou. 2009). However, combined with claims of health impacts, the resulting media accounts led to a confusing assortment of information that resulted in a “media scare” and increased anxiety for residents along the Gulf of Mexico.

In the command post, the perception was that the *in-situ* burning was going to be a larger concern to the public than dispersants. There was a history of dispersant use in the Gulf of Mexico. Burning was a new response technique for the public. Burning is very visible, with potential high human health impacts. Dispersants are fast acting and not easily seen once they moved into the water column. However, it turned out that the burning was viewed more as a “natural” way to remove the oil and the dispersants were seen as adding more chemical into the ocean. The “invisible” threat posed by chemical dispersants to both ecological and human communities increased public fears of new risks in a time of crisis.

There was a suggestion from the EU to bring in sociologist as consultants to focus on the human dimensions of this event. However, that effort was never funded. Human dimensions are not included in the “normal” range of spill management activities. The human dimension aspects of spills are quite nebulous to natural scientists, spill managers, and legal advisors. A study to overcome this would require reaching consensus within the Unified Command and then identifying resources and assignments. This kind of activity, like risk communications, does not align readily with a "next operational period" IAP focus. There was a hope that the incident command could get ahead of the curve and identify which issues would be of highest concern to the local populations and develop methods to deal with them to minimize public fear. Nonetheless, this proposed strategy never materialized and clearly reveals an important lesson for future oil spills. The human dimension should be addressed with high priority and the accurate communication of agency objectives to minimize perceived risks to the public needs to be clearly articulated and implemented.

Since it was difficult to get the media to fully cover the dispersant issue in a fair and representative manner, the Unified Command in Louisiana began a series of local community meetings, which were held in each coastal parish throughout the summer of 2010. These were intended to facilitate improved communications by enabling one-on-one discussions with response specialists and interested members of the community. Members from the response who could directly address specific stakeholder questions staffed approximately 30 tables. The tables addressed a wide variety of topics including vessels of opportunity, safety, wildlife and dispersants. They were staffed by agencies including NOAA, EPA, and Louisiana Department of Environmental Quality. In this manner members of the public were able to meet the people responding and the responders met the people at the parish level. It was successful on a small scale, as each meeting could generally accommodate less than several hundred people.

Open house in Houma, LA. (Photo credit: Ed Levine, NOAA)

One item that became clear from talking to people at these sessions was that they had many misconceptions about dispersants (they did not degrade, they were more toxic than the oil, no one was monitoring the applications, they were being sprayed on people and close to shore, etc.). One statement that provided insight to their concern was "We'd rather deal with the devil we know, than the devil we don't." People in the Gulf are familiar with oil, not dispersants. From conversations with those who visited the dispersant table, it was evident that many people also believed that any oil that was not black must be due to dispersants. Because this oil readily changed from black to brown to reddish-orange as it naturally weathered, people incorrectly assumed that all non-black oil was due to chemical dispersants. Since local fishermen were involved in the response as vessels of opportunity, their photos of the oil, comments, and incorrect assumptions spread quickly *via* social media throughout the Gulf. The fisherman's assumptions combined with social media from trusted community members and further reduced the effectiveness of risk communication efforts. Unresolved concerns about dispersants and their impact on seafood safety and human health persist over a year after the DWH leak was capped.

Risk Communications

The public understanding of risk is closely related to the role of science in characterizing and evaluating risk. A wide variety of risks are viewed as important, while others can be completely ignored. Risk communication is an important response during emergencies. Risk management institutions should include public concerns in the early stages of the response (Pidgeon, et al. 2010:136). The process by which risk, for example, the protection of human health during application of dispersants, is socially defined by science, reflects a complex process referred to as the "social amplification of risk" (Kaperson, et al. 2003). Flows of information are widely available to the public, which provide interpretations of this information involving messages from myriad sources. Among the most important of these sources are scientists, mass media, environmental groups, government agencies, opinion leaders and local authorities. These interpretations ultimately result in the public's assessment of the risk of their behaviors in terms of accepting, ignoring, tolerating or modifying the risk (Kaperson and Kaperson. 2005: 106). Scientific information flows are especially important for the management and communication of "risky" behavior. Nonetheless, public trust in the source of the information flows, sponsorship of scientific inquiry and the clarity of the methodology used by scientists are all important social interpretations that can lead to the acceptance or rejection of scientific opinions.

The negotiation and elaboration of what constitutes the public understanding of risk often occurs in the context of the mass media. It is apparent that the mass media is a prominent source of information regarding technology, science, and risk perceptions. A variety of media sources interpret scientific information, while also framing this information within an organizational context that may include moral and political implications. Therefore, the mass media has both direct and indirect effects on risk perceptions. Given the fact that scientists often provide caveats of uncertainty regarding their information, journalistic accounts often transform this uncertainty to what appears to be "absolute certainty" (Morgan, et al. 2001). Simply put: "The problem in many cases is that when it comes to news coverage the potentiality, uncertainty and ambiguity of risk have to be toned down. Either a risk is truly and surely dangerous or it is not news at all" (Arnoldi. 2009: 131).

The mass media may distort risk by either amplifying certain risks and/or ignoring others. Given that the mass media often poorly communicates the scientific complexity of risks, different media outlets may provide the public with interpretations that reflect their political interests. For example, publications and blogs from environmental organizations raised issues regarding the unknown chemical composition of dispersants, thereby increasing uncertainty regarding exposure risk and seafood consumption. On the other hand, government agencies will report the testing of seafood as comprehensive with their results reflecting a high degree of certainty. When covered by the media, this discourse of contradictory claims also becomes influential for public risk perceptions of the appropriateness and safety of dispersants. The complex scientific questions concerning differences between biota exposure to dispersants and the exposure of seafood to dispersed oil are never addressed adequately by the mass media. This fact often results in confusion and misunderstanding by the public of risks involved with dispersant use.

The perception of the safety of dispersant use involves a complex array of social factors. The public perception of risk involves: 1) how well the risk is understood; 2) how the risk is distributed across various groups; 3) the amount of personal control that can be exerted over risk; and 4) whether the risk is voluntary or involuntary (Morgan, et al. 2001). This information is delivered through a social framework with information flows from a variety of sources including technology, science, and the mass media. Trust, or lack of trust, in the sources of the information presented to the public is also critical for the acceptance or rejection of risk communications. For example, several random surveys of Gulf Coast residents clearly reveal a lack of trust in sources of risk information, including government, corporations and various agencies (Table 1). Research conducted while the DWH was releasing oil (Ulrich. 2011) and five months after the spill (Gill, Picou and Ritchie. 2011) suggest that except for information provided by the Coast Guard, Scientists, and NOAA, very little communication about the spill was viewed as trustworthy by residents of Louisiana, Alabama and Florida. Essentially, there was strong distrust in information provided by BP, the Federal Government, and websites /blogs. The fact that 2 out of 3 respondents did not trust any information released by government agencies, the media and environmental organizations reveals the social context of distrust that characterized risk communications associated with the DWH spill.

Table 1: Trust in Information About the DWH Provided by BP, Government Agencies and Other Sources

Percent of Respondents who Trust:

Coast Guard	79%*	Scientists – 52%**
NOAA	46%	Environmental Orgs. – 37%
FDA	36%	Newspapers – 34%
Local Government	34%	Network T.V. – 26%
EPA	32%	BP – 18%
AL State Government	27%	Websites/Blogs – 12%
Federal Courts	23%	

MMS	22%
Federal Government	17%
BP	13%

*Source of data: Gill, Picou and Ritchie. 2011 **Source of data: Ulrich. 2011

This lack of trust in risk communications regarding efforts to inform the public as to why dispersant application was necessary for the DWH spill and the risk to human health and seafood posed by such use is related to public fears and concerns about dispersants. This fact reveals the importance of trust as it relates to perceptions of risk held by the public. For example, risk managers need to distinguish between “critical trust” and absolute “distrust” of the agency, scientific organization or corporation that is communicating information about the risk of controversy (Pidgeon, et al. 2010). Absolute distrust by people raises important concerns regarding the relationship between the public and the risk management institution. The fact that communications in the early stages of the DWH spill were inaccurate, i.e., amount of oil leaking kept changing and misinformation that BP refused to accept government directives regarding dispersant use, created a social context for public distrust of both the message and source of the message. Given this context, it would have been strategic for all agencies to conduct public meetings to assess public concerns regarding dispersants before providing risk statements on dispersant application and risk (Bier. 2001). Providing more information is often viewed by the public as “business as usual,” resulting in more distrust.

An important issue for effective risk communication is the rebuilding of trust in the public after the threat to residents, tourists or seafood consumers has subsided. Indeed, the use of dispersants following the DWH spill caused health fears among residents and cleanup workers, while also raising concerns throughout the country regarding the safety of Gulf of Mexico seafood. The fact that the public viewed the impact of dispersants as “unknown” increased the perception of risk. When BP and NOAA officials visited primary schools in Louisiana and told children that the dispersants applied to the oil were as safe as laundry detergents, parents angrily responded in disbelief. Once again, by providing “more information” risk managers actually produced more distrust among the public concerning the risk of applying dispersants.

Trust

There are important antecedents to trust. First, trust in an institution requires a perception by the public of organizational competence. Second, a belief in the benevolence of the organization, which reflects a sincere concern of the public’s perspective of the risk. Third, there needs to be a relationship of shared values between the public and the institution (Siegrist, et al. 2010). That is, if a corporation’s values were profit at all cost, then residents who are worried about health issues would not be trusting. This reveals a disconnect between “shared values” (Savadori, et al. 2010). These elements combine to form the important precedent to trust often referred to as “confidence.” Risk communication strategies must include confidence building messages as well as information.

Risk communication often focuses on the dissemination of “facts” to the stakeholders. However, increased knowledge, or the presentation of “facts” by experts is not correlated with increased trust or acceptance of a risk. Actually, when knowledge is limited or such claims contradictory, trust becomes very important for risk communication (Siegrist and Cuetkovich. 2000). When the public is highly knowledgeable about a hazard, they are less reliant on trust for the acceptance of risk. As noted by Siegrist and associates, “confidence is based on familiarity, experience and past performance. Social trust, in contrast, refers to the willingness to rely on others” (Siegrist et al. 2010: 268). When risk communication occurs in a context of no public confidence in the source of the information, there is a reaction of absolute distrust. Risk management institutions need to be knowledgeable about the fears, needs and values of their target audience before communication strategies are deployed (Siegrist et al. 2010: 282). Furthermore, risk communication programs should acknowledge “uncertainty” with a plan to reduce issues of concern. The involvement of representatives of environmental, local citizen and trusted intermediary organizations in the characterization of risk communication facts will also increase public confidence in the message. Indeed, it has been shown that risk communications that strongly argue that health symptoms are not physical, but social psychological in nature, result in a “blaming the victim” public perception. This, in turn, may lead to the rejection of the risk communication message (Wessely. 2000).

Risk communication is a complex process that must involve confidence and trust by the public in the risk management institution. Trust and confidence must be earned through the expression of “shared values” which require equal-status participatory communication strategies. Involvement of environmental groups, local citizen groups and trusted intermediary organizations in open discourse with the public is the first step for organizing effective risk communication concerning dispersant effects on health and seafood safety. Risk management institutions involved in oil spill response should be aware of their public image and attempt to project a positive concern for the public through their organizational culture and their transparent discourse with other stakeholders.

The Consensus Environmental Risk Analysis (CERA) process seeks to bring oil spill decision-makers and their advisors together in US Coast Guard Sectors to review potential response options for use during scenario-based oil spill incidents. Given that for the DWH spill this process was focused on species and habitats present during the scenario period, the consequences for public opinion or the effects on economic conditions was minimized. The future application of this process should identify the reasoning for using or not using different options and find effective strategies to disseminate information to the general public and other stakeholders outside the Unified Command system.

Lingering Issues

- Questions related to this topic that were resolved during DWH:
    - Is it possible to mount a coordinated large-scale dispersant operation?
    - Can you monitor dispersant effectiveness?

  - Was the public affairs unit prepared for communicating risks from dispersants to the public and other stakeholders?

- Knowledge gaps and questions that remained unresolved by DWH:
  - How much is too much?
  - What are the effects on sea life?
  - How long do dispersants remain in the environment?

- New questions that resulted from DWH relative to the topic:
  - How do you explain the issues involved in tradeoffs?
  - How do you build a trusting relationship after a disaster occurs?
  - What are some products that contain similar chemicals to dispersants that people can relate to?
  - How do you maintain, or rebuild, public confidence in seafood safety?

- R&D needed to resolve outstanding questions relative to topic:
  - How can you monitor for effect in a more real-time mode and translate the results to risk communications for public health and safety?
  - How can you build shared values during a spill response?
  - How do you plan for and recognized the human dimensions of oils spills?

Conclusions

The lessons learned from the DWH spill provide information across a broad array of concerns associated with large-scale oil spills. An effective, coordinated large-scale dispersant operation was mobilized following the DHW blowout. A monitoring system that detailed the effectiveness of both surface and subsurface applications was designed and applied throughout the spill area. Present research efforts are collecting scientific data on the impacts of dispersants on marine habitats and sea life. Questions regarding impacts and the degradation process of dispersants in the marine environment will also be addressed by these on-going scientific studies. At this time, the risks posed to the environment and human health by the dispersant applications in the Gulf of Mexico appears to be minimal. Nonetheless, public opinion continues to challenge such contentions.

The lessons from the DHW spill also identify new questions and research needs directly associated with risk communication issue that emerged over the spill timeline and continue to the present. First, risk management institutions should anticipate “media scares,” the reporting of contradictory information and a general lack of accurate information for the scientific basis of procedural decisions made by the unified command system. The confusing context of the mass media, including social media sites, identifies a challenge for risk management institutions that involves broadening the participatory discourse of risk communications, building trust in information provided to the public and acknowledging the uncertainty of risks when appropriate. Risk management institutions need to be familiar with the economic, social and cultural characteristics of communities impacted by oil spills. The importance of the human dimension for responding to oil spills became apparent in the months following the DHW incident.

The fact that some limited success in communications regarding dispersants and their use was achieved at small community meetings attests to the importance of understanding public concerns and fears prior to providing risk communication “facts” from the United Command. The participation of trusted intermediary organizations, such as Sea Grant, environmental organizations, public officials, etc., in these gatherings would also provide a mechanism to establish “shared values” between spill response organizations and residents of impacted communities. This process would result in positive trust building activities which enhance public acceptance of risk communication information.

There are also continuing problems regarding public perceptions of seafood safety, water quality, air quality and other ecological risks associated with the aftermath of the DWH release of over 200 million gallons of oil into the Gulf of Mexico. The human dimension of oil spills projects a number of economic, social, cultural and legal issues well into the future. Although the DWH spill is physically over, consequences for the human dimension will persist. Future basic research on risk perceptions regarding seafood safety and human health are needed and applied programs on the effective delivery of important risk information should be implemented at the community level. People continuously reflect on risk behaviors and risk perceptions do change over time. Because of this fact, efforts to build trust in risk management institutions through participatory discourse within local communities should be a high priority for fostering recovery. Given that social surveys show that the Coast Guard, reports from scientists and NOAA were the most trusted entities for the Gulf Coast residents identifies three important sources for sponsoring and implementing future risk communications about the lingering consequences of the DWH spill.

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Oil Dispersants and Human Health Effects

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Introduction & Background

The explosion and subsequent blowout of the Deepwater Horizon (DWH) offshore drilling rig on April 20, 2010, led to the largest accidental offshore oil spill since the advent of the petroleum industry, dwarfed only by the deliberate release of crude oil by Iraqi forces during the Persian Gulf War. Over the time until the well was capped on July 15, approximately 200 million gallons of oil spilled into the Gulf of Mexico from the ocean floor beneath the well site located approximately 50 miles off the coast of Louisiana. For perspective, this amount is nearly 20 times the amount of oil discharged during the Exxon Valdez incident in Alaska. As a result, massive mitigation efforts took place during and after the flow of oil which entailed mechanical recovery, controlled burning, and chemical dispersion. As a result unprecedented application of oil dispersant agents was employed by BP during this time until their use was curtailed by the EPA on May 26, 2010. Overall, about 17 - 20% of the crude oil was mechanically recovered and 6 – 8% burned. For the oil remaining in the environment, about 40% (of original input) was evaporated, dissolved, or dispersed into small droplets by natural processes. Initially, it was estimated that only 16.5 million gallons of oil (<10% of total spill) were dispersed into the environment by chemical means, however this approximation was revised upward by 2-fold. The unaccounted for percentages of original oil presumably remain on the surface or washed on shore[1].

Oil dispersants are chemical mixtures of surface active agents and solvents designed to combine with large floating masses of oil and facilitate the dispersion of the oil into small microscopic droplets that then disperse throughout the water column. The micro-sized oil droplets can then be carried and diluted into the open ocean rather than wash ashore or adhere to wildlife and marine equipment. While it is assumed that dispersed oil is more readily degraded by microbial or physical processes, it can also increase the bioavailability of oil constituents and alter routes and extent of exposure to various toxic chemicals contained in the oil.

Potentially hazardous constituents of concern in dispersants

Currently there are 12 oil dispersant products approved for use by the US EPA and the chemical composition of most remains proprietary information. Even when the specific chemical ingredients are made available, the precise proportion of each entity contained in the product mixture is either not declared, or else specified only over a rather broad range. Table 1 lists these products along with their ingredients, if available. It is estimated that over 1.8 million gallons of

COREXIT 9500 and COREXIT 9527 were applied during these efforts, including the novel deepwater use of about 800,000 gallons injected below the ocean surface in an attempt to intercept the gushing oil plume located near the source. Early on in the mitigation effort COREXIT 9527 was used, however, due to limited on-hand availability, COREXIT 9500 was substituted as the primary product employed. It remains unclear as to how much of each particular product was used. As the crisis unfolded public perception and opinion became concerned with the additional threat to the environment and human health posed by application of hazardous chemicals in dispersants, as well as the toxic components within the oil itself. The initial withholding of information concerning the chemical composition of the dispersant contributed greatly to public concern. Identification of specific ingredients allows some estimation of their potential toxicity, however, it must be emphasized that human exposures to oil dispersants represent exposures to complex mixtures of the specific ingredients, as well as, in combination with oil components. Much less information is available regarding how such combinations of chemical agents might interact.

Broadly, the potentially hazardous effects represented by the oil dispersants can be divided into two classes. The first are direct toxic effects of the agents contained in the oil dispersant product. The second is the potential to modify the environmental deposition and/or bioavailability of toxic principals within the oil itself. This will be discussed in more detail below. It is difficult to comment on the specific ingredients contained in the products whose formulation remains a trade secret. We can, however, provide some insight regarding those whose formulation is known and, in fact, represent those used almost exclusively in the DWH incident (COREXIT 9500 and 9527). Therefore, we will restrict our discussion primarily to the following specific chemicals: Dioctyl sodium sulfosuccinate, 2-butoxyethanol, 1-(2-butoxy-1-methylethoxy)-2-propanol, and ethoxylated alcohols. Some of the products also contain various petroleum-derived products. For example, COREXIT 9500 contains a large amount (10 – 30%) of hydrotreated light petroleum distillate (CAS #64742-47-8), which contains primarily C_9 – C_{12} saturated paraffinic hydrocarbons with less than 1% aromatic hydrocarbon content. Other distillate fractions employed as solvents may contain varying amounts of additional aliphatic and aromatic compounds depending on the distillation process. Numerous toxic effects, including malignancy, on a variety of target organs including central nervous system, lung, skin, liver, and bone marrow have been established for several of these components and thus they can contribute to the overall burden of toxic chemicals released during the DWH incident. Since, however, these chemicals are also present as components of the crude oil itself, we will limit our further discussion of toxicologic profiles to those agents specific to the dispersants. Sorbitan octanoate and its polyoxyethylene derivatives, used extensively as food and cosmetic additives, appear to be relatively non-toxic, aside from occasional reports of hypersensitivity and will not be discussed further. They may, however, like other surface active agents, contribute to the ability of dispersants to modulate exposure to oil components. We present here primarily toxicity data pertinent to single agents, however, it is important to remember that dispersants are complex mixtures and, thus, the potential for interactions between individual components is high, yet difficult to predict.

Dioctyl sodium sulfosuccinate (DSS) (IUPAC: Sodium 1,4-bis(2-ethylhexoxy)-1,4-dioxobutane-2-sulfonate) (CAS #577-11-7) is an anionic surfactant and a common ingredient in several household products. It is best known as the active ingredient contained in many over-the-counter stool softeners and laxatives (ex. Colace™, Ducosoft™, Ducolax™, Ex-lax™ stool softener among others). As such it is usually taken orally but can also be given by rectal enema. The recommended daily dose is between 50 and 200 mg (0.7 – 2.9 mg/kg b.w.) with up to 500 mg/day sometimes used. It also has been used as a pesticide on grapes, oranges, feed corn, almonds, nectarines[2]. Systemic absorption after oral administration has been documented in humans[3], but its extent has not been well studied. Absorption in the rat appears extensive with subsequent metabolism and combined urinary (60%) and biliary (40%) excretion. Some concern has been given regarding the potential to produce 2-ethyl-hexanol as a metabolite but so far this pathway appears to be nominal[3b, 4].

Most of the untoward effects seem to be mechanism related and usually manifest as gastrointestinal symptoms including bloating, diarrhea, cramping, GI upset/pain. Prolonged use in the face of such symptoms can conceivably produce dehydration and electrolyte imbalances. The acute LD_{50} in mice ranges from 1.5 g/kg[5] to 4.8 g/kg[6]. The LD_{50} in guinea pig was only 0.65 g/kg and horses appeared similarly susceptible to the adverse effects of the drug[7]. Cause of death was hypovolemic shock and circulatory collapse attendant with loss of fluid into the intestinal lumens, thus is essentially related to the mechanism of its therapeutic action. Several prolonged exposure studies similarly noted GI changes, however, consistently failed to show any changes in other systemic organ systems[8]. No evidence appears that DSS is carcinogenic. Chronic feeding of DSS (1% of diet) failed to show any promotional activity of tumors induced in response to 1,2-dimethylhydrazine (20 mg/kg/week, s.c) and, in fact, reduced the number of tumors seen at lower doses of initiator (10 mg/kg/week, s.c)[9]. In a three generation feeding study in rats 0.5 and 1% DSS in the diet caused a reduction in body weight, however, reproductive performance remained normal throughout the study and no treatment-related macroscopic changes were observed[10]. In a retrospective study where 6,937 women were prescribed drugs during the first trimester of pregnancy, 473 received DSS with only a single birth of a child with an unspecified congenital disorder[11]. Allergic hypersensitivity reactions have been reported[12] but the incidence of anaphylaxis appears low. As reported by eHealthMe.com, a website that tracks post-marketing adverse event reporting to the FDA, only one case of anaphylaxis was reported out of the 411 people who reported side effects to Colace™[13]. Prescribing information for products containing DSS warn against concomitant use of mineral oil since therapeutic doses of DSS may enhance systemic absorption of mineral oil. This effect serves as a harbinger of the possible toxic interactions between oil dispersants and oil components.

2-Butoxyethanol (2-BE): 2-BE (CAS #111-76-2) (ethylene glycol monobutyl ether, monobutyl glycol ether, Butyl CelluSolve™, Dowanol™ EB) is a high-production volume solvent in the chemical class of glycol ethers. The structural formula of 2-BE is $CH_3CH_3CH_2$-O-CH_2CH_2-OH.

It is a member of a larger class of ethylene gycol ethers that include 2-methoxyethanol and 2-ethoxyethanol, as well as higher series of ethoxylated fatty alcohols. 2-BE is widely used in the manufacture of various enamels, lacquers, paints and other surface coatings. In addition, it is also commonly found in a variety of household cleaners and products. Because of its relatively high vapor pressure it can exist in the atmosphere as a vapor. 2-BE is also easily miscible in water and most organic solvents. Because of its aqueous miscibility, the propensity to produce a vapor phase is reduced upon addition to water. As such, the primary routes of exposure thought to be of concern are respiratory and dermal, although accidental/intentional ingestion of some 2-BE containing products have been documented. 2-BE can be readily absorbed via all three major routes of exposure. In fact, percutaneous absorption through the skin is thought to be a significant route of exposure for vaporous 2-BE within the atmosphere[14]. In addition, it appears that 2-BE is much more efficiently absorbed from an aqueous solution applied to the skin compared to an equivalent dose applied as a neat solution[15]. While most of the dispersant products are recommended for use as undiluted solutions for aerial application, others like COREXIT EC7664A, a surface washing agent, are applied as a 1- 3% diluted solution[16]. Boat spraying of COREXIT 9500 and 9527 products requires specialized low-pressure low-volume pumps, which if unavailable, may necessitate use of diluted product down to 5 – 10%.[17]

The metabolism of 2-BE proceeds mostly through typical alcohol and aldehyde dehydrogenase pathways with formation of 2-butoxyacetaldehyde and 2-butoxyacetic acid (2-BAA), the principal metabolite[18]. This raises the possibility of competitive inhibition of metabolism by other primary alcohols like ethanol and altered kinetics during consumption of alcohol. Administration of ethanol to rats significantly increased blood levels of various ethylene glycol ethers after their inhalation[19]. At higher concentrations this pathway is likely saturated and alternate pathways of O-dealkylation and glucuronidation become more quantitatively important[18b]. An amino acid conjugate, n-butoxyacetylglutamine, has been identified in humans but not experimental animals[20].

The principal health effect of 2-BE observed in humans is central nervous system toxicity with additional kidney and liver injury at high doses. 2-BE can produce an acute CNS syndrome typical of exposure to other organic solvents consisting of dizziness, nausea, vomiting, loss of coordination, ataxia, confusion, depression, loss of consciousness. Severity is related to the dose. 2-BE is also an irritant to mucosal surfaces and skin, therefore ocular, oro-pharyngeal, nasal, respiratory, and dermal symptoms are also observed. 2-BE does not appear to be a skin sensitizer in humans[21].

Acute LC_{50}s or LD_{50}s have been established in several species and are summarized in Table 2[22]. Much of the concern regarding 2-BE stems from its established ability to produce profound intravascular hemolytic anemia in experimental animals. This effect is characterized by a decreased number of circulating red blood cells (RBCs) and elevations in free hemogoblin. Free hemoglobin is believed to be responsible for the observed tissue damage especially in the kidneys and liver. Inhalation of 2-BE by female rats (62 ppm, 299 mg/m^3) for 4 hrs increased osmotic fragility of erythrocytes[23]. This effect has been documented repeatedly in multiple species including dog, rabbit, and with both acute and longer term-exposure[23-24]. Older rats appear more sensitive than younger animals[25], as well as female compared to male rats[26]. These observations likely reflect the greater accumulation of the metabolite 2-BAA in both sensitive groups (see below)[25, 27]. In vitro studies using isolated erythrocytes have provided important insights into 2-BE induced hemolysis. The 2-BAA metabolite of 2-BE appears to be the primary offending species for these effects since in vitro incubation of isolated red blood cells with BAA produced hemolysis at between 20 – 40-fold lower concentrations than the parent compound[24b, 28]. Importantly, the same studies observed marked species differences in sensitivity to the hemolytic effects. Human RBCs were markedly more resistant to these effects than rats[24b, 28] requiring nearly 10 times more BAA to produce hemolysis. Other sensitive species include mice, hamsters, rabbits, and baboons, while resistant species include pigs, dogs, cats, and guinea pigs[29]. These species differences in part reflect intrinsic differences in the red blood cells themselves, presumably at the level of membrane composition. 2-BE-induced frank hemolysis is rarely reported in humans, even during severe poisonings following suicide attempts (ingestion of 25 – 60 gm)[30]. Occupationally relevant exposures (100 ppm) could produce headache and vomiting but no signs of hemolysis, although higher exposures have been shown to alter osmotic fragility when tested in vitro[23, 31]. During a controlled human exposure study, vomiting and headache were observed after breathing 100 ppm (483 mg/mm^3) for 8 hrs. No clinical signs of hemolysis were observed at any level although exposure to 195 ppm (942 mg/m^3) did increase osmotic fragility of RBCs when assessed in vitro[23]. After in vitro incubation of human RBCs with 2 mM BAA, a concentration which causes complete lysis rat RBCs, Udden observed no changes in morphology or deformability even in cells derived from patients with hereditary spherocytosis, a disorder characterized by red cells with high osmotic fragility, and sickle cell disease[32].

Reproductive toxicity (both male and female) has been observed with the related glycol ethers, 2-methoxyethanol and 2-ethoxyethanol, however, 2-BE appears relatively devoid of reproductive and developmental effects. No testicular effects were observed in rodents exposed to 2-BE by inhalation of 800 ppm for 3 hrs[33] or oral administration of up to 2000 mg/kg/day, 5 days/week, for 5 weeks[34]. Developmental studies exposing pregnant dams to 2-BE by a variety of routes failed to show any fetotoxic or teratogenic effects except at doses that produced significant maternal toxicity[35]. While in vitro tests for mutagenic and genotoxic effects have yielded equivocal results[36] in vivo tests have been largely negative. 2-BE was negative in the bone marrow micronucleus test after i.p. administration in rats and mice[36c, 37]. Using [^{32}P]-post-labelling assay, no DNA adducts were observed in multiple organs of orally dosed-rats[38]. Keith et al. showed no effects on DNA methylation in multiple organs and tumor formation in FVB/N transgenic mice[38]. 2-BE has been associated with formation of hemiangiosarcomas in liver and other organs of mice[39], however, these tumors are now thought to arise secondarily through the heme-dependent generation of reactive oxygen species and hypoxia-dependent proliferative signaling in endothelial cells, which arise during the hemolytic destruction of RBCs[40]. Since these tumors appear only in the context of profound hemolytic effects, they are thought not to be of significance in human exposures.

1-(2-butoxy-1-methylethoxy)-2-propanol (CAS # 29911-28-2), more commonly referred to as dipropylene glycol n-butyl ether (DPnB), is a component of both COREXIT 9500 and 9527. Synonyms for this compound include 2-(butoxypropoxy)-2-propanol, dipropylene glycol monobutyl ether, ARCOSOLV™ DPNB, or DOWANOL™ DPNB. DPnB is also a glycol ether, except it is classified as a P-series glycol ether (synthesized from propylene oxide) unlike 2-BE discussed above whose synthesis is based on ethylene oxide (E-series) as the starting material. In general, the P-series glycol ethers are frequently considered safer alternative to E-series compounds as they lack the hemolytic toxicity and appear to have less potential to disrupt reproductive function and fetal development[41]. Little of the descriptive toxicology, however, appears in the peer-reviewed literature but instead relies upon industry-sponsored unpublished studies. DPnB (Table 2), as well as other propylene glycol ethers, have very low acute toxicity with LD_{50}s greater than 1,800 mg/kg in oral studies, 2,000 mg/kg for dermal exposures, and >250 ppm for inhalation exposures[42]. In many cases, the actual LD_{50} were not obtained within the dose range employed. When signs of toxicity were observed, they usually included generalized CNS and respiratory depression common with exposure to other solvents. DPnB was classified as ”slight irritating” to skin and eyes[43], but no evidence of sensitization was observed[44]. An intriguing peer-reviewed study, however, has recently appeared that begs further consideration. Choi et al. [45] conducted a case-control study correlating household levels of different classes of indoor air volatile organic compounds (VOCs) with allergic disease and IgE sensitization. Of the 8 different classes of VOCs including aromatic hydrocarbons, aldehydes, organic acids, and others, only the propylene glycol and glycol ethers were associated with increased risk of multiple allergic symptoms and atopy. Therefore, the association of glycol ethers to asthma and other allergic diseases deserves further attention although the actual offending chemical(s) have not been identified.

Longer term exposure studies also revealed relatively benign effects. Two-week inhalation studies in rats exposed to DPnB demonstrated a threshold for toxicity somewhere between 320 mg/m^3 (40 ppm) and 810 mg/m^3 (104 ppm)[46]. Toxicity manifested primarily as histopathological lesions in the liver and nasal mucosa. In this regard, DPnB appears slightly more toxic that other propylene glycol ethers such as propylene glycol n-butyl ether[47]. [47c]Dermal exposure to rats for up to 13 weeks produced some localized skin irritation at all doses but little in the way of systemic toxicity except small decreases in body weight and elevated neutrophil counts with a NOAEL of 0.1 ml/kg-day (91 mg/kg-day) and LOAEL of 0.3 ml/kg-day (273 mg/kg-day)[48]. Prolonged oral exposure (13 weeks) produced slight elevations in liver and kidney weights without histopathology and mild changes in clinical chemistries only at the highest dose tested (1,000 mg/kg/day)[49]. Importantly, these studies, as well as one specifically designed to test hematological effects[50], demonstrated that propylene glycol ethers do not share the hemolytic effects manifest by their E-series relative, 2-BE, as discussed above. Functional reproductive studies with DPnB have not been carried out but no changes in the reproductive organs were observed at necropsy in any of the repeated dosing studies listed above and reproductive endpoints after exposure to the structurally-related propylene glycol monomethyl ether[51] were negative. Developmental studies during dermal exposure of rats established a LOAEL of > 910 mg/kg/day (the highest doses applied in each study), respectively, for maternal toxicity, embryo-/fetal toxicity, or developmental aberrations[52]. In most studies DPnB is not mutagenic by in vitro or in vivo assays[53], however, three tests all from a single laboratory showed chromosomal aberrations in CHO cells[54]. National Toxicology Program testing for carcinogenic effect of the related agent, propylene glycol monobutyl ether, observed an increase in hepatic tumors in male and female mice, but not rats exposed to 1,200 ppm by whole-body inhalation (the highest dose tested) for 2 years[55]. Male mice showed exposure-related increases in non-neoplastic lesion in the kidney with equivocal increases in renal neoplasia. DPnB has not been similarly tested for tumorigenic potential in long-term studies. Therefore, with the paucity of in vivo data, as well as, equivocal in vitro results, formation of hepatic lesions with preneoplastic potential, and tumorigenic effects of structurally-related compounds, labeling DPnB as non-carcinogenic should be taken with some caution.

One likely explanation for the dramatic differences between the structurally similar 2-BE and PGBE relates to differences in metabolism. It is believed that the major offending species for hematologic and reproductive toxicity seen with the E-series glycol ethers is the corresponding acid produced during in vivo metabolism by alcohol and aldehyde dehydrogenases (2-butoxy acetic acid in the case of 2-BE). The major species (>95%) contained in commercial preparations of PGBE, however, is the alpha isomer which represents a secondary alcohol, thus is not a substrate for alcohol dehydrogenase and incapable of forming an alkoxypropionic acid. Instead, metabolism of PGBE proceeds largely by typical mixed function oxidase-dependent O-dealkylation yielding *t*-butanol and propylene glycol. Propylene glycol is readily converted to lactate and pyruvate for consumption in the Krebs cycle. *t*-butanol, as well as some of the parent compound, is excreted as a glucuronide conjugate[56].

Ethoxylated alcohols deserve a brief mention here in that they are chemically related to simpler glycol ethers. They are usually composed of a long chain fatty alcohol (C_8 – C_{15}) linked to a polyethelyene glycol chain also of varying length (1-20). Modulation of the length of the carbon chains as well as the number of ethoxy units can be used to determine specific properties of these non-ionic surfactants. One of the approved oil dispersant products, DISPERSIT SPC 1000 contains ethoxylated alcohol specified as a mixture of C_{12} – C_{14} fatty alcohol without noting the relative degree of ethoxylation. While these chemicals have undergone considerable scrutiny in terms of their potential environmental toxicity, there is very little information regarding their effects on humans or other mammals. Various MSDS sheets for these compounds note them to be significant irritants upon ocular or dermal exposure, but no long term systemic toxicities are reported at typical usage exposures. One possible issue to consider is the fact that atmospheric (and perhaps microbial) oxidation of these chemicals can give rise to reactive aldehydes with potential to produce contact sensitization and subsequent allergic reactions upon re-exposure[57].

Secondary effects by altering oil component exposure

Crude oil represents a complex mixture containing a vast array of aliphatic and aromatic hydrocarbons, heavy metals, and other substances. The total petroleum hydrocarbon (TPH) fraction represents the greatest concern to human health. Depending on the carbon chain length or number of aromatic rings each compound has its unique profile of volatility, solubility, and physical-chemical properties that ultimately determine its toxicokinetics and toxicodynamics. The low-molecular weight BTEX fraction (benzene, toluene, ethylbenzene, xylene) is of concern because they can diffuse into aqueous media as well as readily volatalize from a surface film of oil. The carcinogenic effects of benzene are well-known as a leading cause in acute myelogenous leukemia[58]. Larger molecular weight species (naphthalene, benzopyrene) may remain more associated with the crude oil mass, but still possess toxic potential. An actual description of the specific adverse health effects of TPH is beyond the scope of this discussion, but the interested reader is referred to ATSDR profile for Total Petroleum Hydrocarbons[59].

Perhaps, the biggest question regarding the action of oil dispersants is how they might modulate the fate and transport of various oil constituents within the environment. By their nature they are designed to break up the oil mass into tiny micro-sized droplets that remain suspended within the water column rather than form a “slick” on the water surface. Wave tank experiments indicate the size of chemically-dispersed oil droplets to be in the 10 – 50 µm range with some even smaller, although the size of oil droplets formed over time after application of dispersants in the natural setting of an accidental spill is not well studied[60]. This might reduce the evaporation of BTEX components, for example, reducing atmospheric concentrations and thus inhalational exposure. The concentration of these species, as well as heavier compounds, however, are now also increased within the water, and may promote exposure via dermal contact (swimming, water-on-skin exposure during clean-up operations, aerosol generation during wave action), as well as increasing the possibility that such chemicals might sequester in various marine biota because of their potential to bioaccumulate. Such physical dispersion of the oil mass into an emulsion of microscopically-sized particles dramatically increases the surface area of the overall oil-water interface where diffusion and absorptive processes proceed. The absence of a distinct odor of volatile oil components, as well as visual evidence of an oil slick could also impart a false sense of security when it comes to use of personal protection equipment such as respirators/filters, gloves, and other body coverings.

Of note is the hypothesis that the presence of oil dispersants can also directly affect how various chemicals enter the body. Again the increase in surface area whereby oil-derived chemicals might contact the skin and lung lining might facilitate absorption by the dermal and inhalation routes. We mentioned above that water mixtures of glycol ethers showed enhanced dermal absorption above that seen when glycol ethers are exposed neatly to the skin[15], however, the dermal absorption of dispersed TPH components has not been compared to those in undispersed oil. DSS, under the trade name Aerosol-OT, has received recent attention as a means to enhance oral absorption of various pharmaceuticals and is the subject of patents for improved drug-delivery systems[61]. DSS enhanced the efficacy of tetracycline on various microorganisms, including some normally resistant to the drug, by enhancing intracellular permeation of the drug[62]. Aerosol OT/1-butanol emulsions were also found to markedly enhance penetration of the antibiotic, clindamycin phosphate, through human epidermis when compared to a 70% isopropanol vehicle[63]. The ability of Aerosol OT to similarly enhance diffusion of 5-fluorouracil through skin was accompanied by modifications in the lipid structure and degree of hydration of the stratum corneum layer of the skin[64]. Thus, it is entirely possible that DSS and various other surface active agents in dispersant products can enhance absorption of specific TPH components and thus potentiate any adverse effects resulting from such exposures. Because of its volatility, most benzene applied to skin is expected to evaporate before substantial systemic absorption. If, however, benzene is sequestered into an emulsified aqueous suspension by the action of dispersants its potential for evaporation and, therefore, dermal absorption might be modified. While direct administration of DSS (1%) into the lungs of dogs produced some pulmonary edema[65], DSS aerosols (5%) accelerated lung clearance of the tracer, ^{99}Tc-diethylenetriamine pentaacetate (^{99}Tc-DPTA) without affecting gas exchange or lung mechanics[66]. In fact, DSS has been considered as a means to enhance delivery of pharmaceutical agents via enhancing alveolar absorption[67]. In rabbits, DSS successfully enhanced the absorption and biological action of insulin delivered by aerosol inhalation[68].

Probable exposure scenarios and possible at-risk groups

It is expected that those individuals directly involved with the clean-up operations and direct handling/application of the dispersants would have received the highest exposure and, therefore, are the most at risk for adverse effects. In these cases their most likely route of exposure was via inhalation or dermal absorption. The National Institute for Occupational Safety and Health conducted a limited series of health hazard evaluations for several groups of responders employed during the spill clean-up[69]. The most commonly reported symptoms were headache, upper respiratory symptoms, and symptoms related to heat stress. While workers who reported exposures to oil and dispersants reported higher prevalence of all types of symptoms, no assignment of specific causative agents could be made. Health symptom surveys taken aboard two vessels actively engaged in releasing dispersants were similar in scope and magnitude to those obtained from other workers who had not worked on boats and had no exposures to oil or dispersants. Personal breathing zone and area air sampling was used to evaluate exposure to a variety of chemicals, including propylene glycol, a COREXIT component, and measured levels that that were consistently below the acceptable occupational exposure limit (OEL). Moreover, NIOSH investigators consistently noted that workers generally complied with wearing the necessary personal protection equipment required for the task at hand.

Local populations residing on the shores are likely at minimal risk for toxicity based on dilution of the chemicals in surrounding water and air. Aerial application of dispersants occurred only at distances greater than 3 miles from shore and serves to severely limit respiratory and dermal exposure on the shoreline. Some concern has been raised about potential contamination of seafood with chemical dispersants. The environmental half-life of these compounds is short and there is little evidence that any of the chemicals discussed above appreciably bioconcentrate or accumulate within the food chain. Trace levels of DSS measured in seafood samples tested after the opening of previously closed waters were considered insignificant to human health by the FDA.

As always the primary at-risk groups based on the limited knowledge we have are the very young, the elderly, and those with preexisting conditions especially chronic lung disease. The clean-up worker investigation conducted by NIOH noted a disproportionate number of smokers among the clean-up workers[69]. Pregnant and nursing women should also be advised to minimize potential exposure simply as a matter of common sense. It is possible that the capacity for metabolism can also determine sensitivity. For example, individuals who possess high levels alcohol dehydrogenase activity (those of Asian or Amerindian descent, for example) might actually be sensitive to some of the effects of 2-BE compared to others with less functional capacity to generate the more toxic metabolite, 2-BAA. Similarly, genotypic/phenotypic variability in the cytochrome P450(s) responsible for O-dealkylation of propylene glycol ethers could contribute to alterations in the physiological disposition of P-series glycol ethers. No specific studies, however, have addressed these issues.

Perceived Safe Levels

No environmental or occupational regulatory/occupational standards for air or water exist for DSS. Because of its use as an OTC medicine and possible application of as food additive, the Acceptable Daily Intake as set by the WHO Joint Expert Committee on Food Additives is 6 mg/person/day and that set by the U.S. FDA is 30 mg/person/day. As a stool softener the recommended adult doses are in the range of 100 – 500 mg/day and appear to be well tolerated over extended periods of time. Because of their high vapor pressures, regulatory guidelines have been set for the glycol ethers. The following air standards for 2-BE have been set: TLV TWA (Threshold Limit Value, AIGIH) = 25 ppm, PEL (Permissible Exposure Limit, OSHA) = 50 ppm, and IDLH (Immediately Dangerous to Life or Health, NIOSH) = 700 ppm. No limits have been set specifically for DPnB, but those corresponding to dipropylene glycol monomethyl ether are TLV =100 ppm and STEL (short-term exposure limit, ACGIH) = 150 ppm.

Potential relevant biomarkers and future studies

It will be a challenge to ascertain whether the application of oil dispersants into the Gulf of Mexico will have any perceptible effects on human health. The NIH-sponsored Gulf Long term Follow-up (GuLF) Study, led by NIEHS, is set to begin to study clean-up workers and volunteers to understand the scope and diversity of adverse health effects amongst those individuals most highly exposed to the toxic agents in question. One of its major challenges, however, will be to accurately characterize and quantify exposure to specific oil and dispersant chemicals alone, as well as in mixtures. Clearly, one of the prime issues will be to determine specific populations who were exposed to these agents and quantify the extent of their exposure in terms of time and amount. Detailed clean-up worker histories might allow grouping of workers based on their proximity in time and space to actual application of dispersants and comparing their ultimate health outcomes to oil clean-up workers with similar tasks in regions where dispersants were not applied. Clearly, a more accurate way to document exposure (an internal dose) would be to measure parent compounds or their metabolites in biological samples (blood, urine, other). However, the pathways of metabolism of DSS are not well described. Measurement of urinary 2-BAA has proven useful in monitoring employees potentially exposed to 2-BE in other settings[70]. It is important to remember, however, that these approaches are most useful only in the early stages following exposure since the compounds are presumably cleared fairly rapidly in the absence of a continuous exposure source. Moreover, there clearly are other sources of exposure for these agents such as laxative use and various household cleaning products containing glycol ethers. Therefore, for local residents not directly involved in clean-up activities, the background levels of exposure to many of these agents from other sources may approximate, or even exceed, those specifically from dispersant use. While biomarkers of effect would be useful, there are relatively few, if any, specific for these compounds. Measurement of RBC osmotic fragility could be used to monitor the hemolytic signature effect of E-series glycol ethers, but recall that humans are amongst the least sensitive species for this effect. Various measures of DNA damage and adduct formation in peripheral blood cells has provided some utility in measuring potential genotoxic effects after other oil spills.

The most fruitful future studies might be in regard to studying the interactions between oil dispersants and specific TPH components within the oil itself. Some chemicals in TPH might be more persistent than the dispersant chemicals so measurement of body burden with and without dispersant exposure might prove informative. Animal and in vitro studies that address availability and toxicity of TPH components in the presence and absence of dispersants should be carried out. For example, does simultaneous inclusion of dispersants in TPH component feeding studies alter the genotoxic and tumorgenic effects? Direct in vitro studies can easily be performed to determine if DSS or other oil dispersant components can increase permeation of oil components across skin. Human skin models employing cadaver-derived or tissue-engineered skin are routinely used to assess xenobiotic transport across this barrier in specifically-designed diffusion barrier chambers.

As pointed out earlier, the dispersant products themselves represent complex mixtures whose toxicity may not be adequately predicted by knowledge of the single ingredients alone. Few studies have directly tested the dispersant products for toxicity. Recently, the irritant and sensitizing properties of COREXIT 9500A and DSS were compared in a dermal application model in rats[71]. COREXIT was found to be about 10-fold more potent than would be expected based in its content of DSS alone. Acute 5 hr exposure of rats (27 mg/m^3) of COREXIT aerosols was found to induce a small change in lung compliance without inflammation[72] and changes in peripheral vascular reactivity[73]. These effects, however, were transient and extrapolation of the exposures conditions to those encountered in the real world is problematic.

Summary

The massive deployment of oil dispersants in the Gulf of Mexico in response to the DWH oil spill has raised concerns regarding their potential adverse effects to the environment and human health. The specific ingredients contained in many oil dispersant products remain proprietary information, however, those contained in COREXIT 9500 and COREXIT 9527, the products used almost exclusively in the Gulf, were available for review. Exposure of the general populace of Gulf shore to the major ingredients dioctyl sodium sulfosuccinate, 2-butoxyethanol, propylene glycol butyl ether, and other ethoxylated alcohols should be considerably below the range expected to produce adverse effects based on a review of their toxicological profiles. Of note, however, is the severe paucity of both human and laboratory data regarding the potential effects of chemical mixtures as represented by oil dispersant products. Those individuals involved in clean-up operations that directly handled oil dispersants or worked in the immediate area of application probably encountered greater amounts of dispersants and might a greater risk of adverse effects, but, in general these should be mild and self-limiting. Importantly, for several of the major toxicities described in experimental animals, humans appear to comparatively resistant. Perhaps a greater question pertains to the ability of dispersants to alter the toxicological properties of the chemicals contained in the oil itself. By their nature they are designed to alter the fate and transport of crude petroleum and its constituents and, therefore, can change the route and extent of human exposures. The physico-chemical properties of petroleum hydrocarbons contained in micro- -sized oil droplets desperately needs to evaluated and compared to petroleum hydrocarbons alone, in simple aqueous solution, and in air. Moreover, some the oil dispersant products themselves have potential to directly modify biological barriers and, thus, alter permeation of oil-derived chemicals at various routes of exposure.

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Table 1. Approved Oil Dispersant Products and Their Ingredients

Product	**Ingredients**
BIODISPERS (Petrotech America)	Proprietary
JD-109 (GlobeMark Resources Ltd.)	Proprietary
JD-2000 (GlobeMark Resources Ltd.)	Proprietary
NOKOMIS 3-AA (Mar-Len Supply, Inc.)	Proprietary
NOKOMIS 3-F4 (Mar-Len Supply, Inc.)	Proprietary
COREXIT 9500 (Nalco Energy Services)	Sorbitan, mono-(9Z)-9-octadecenoate Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2- ethanediyl) *derivs*. Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) *derivs.* **Butanedioic acid, sulfo-, 1,4-bis(2-ethylhexyl) ester, sodium salt (Dioctyl sodium sulfosuccinate)** (10 – 30%) **1-(2-butoxy-1-methylethoxy)-2-propanol** (1 – 5%) Distillates (petroleum), hydrotreated light (10 – 30%)
COREXIT 9527 (Nalco Energy Services)	Sorbitan, mono-(9Z)-9-octadecenoate Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) *derivs.* Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) *derivs.* **Butanedioic acid, sulfo-, 1,4-bis(2-ethylhexyl) ester, sodium salt (Dioctyl sodium sulfosuccinate)** (10 – 30%) **1-(2-butoxy-1-methylethoxy)-2-propanol** (1 – 5%) Distillates (petroleum), hydrotreated light **2-Butoxy-ethanol** (30 – 60%)
MARE CLEAN 200 (Taiho Industries Co. Ltd.)	Poly(oxy - 1,2 - ethanediyl), α- hydro - ω - hydroxy - , ether with 1,2,3 - propanetriol (9Z) - 9 - octadecenoate Poly(oxy - 1,2 - ethanediyl), α- (9Z)- 1 - oxo - 9 - octadecen - 1 - yl - ω- hydroxy- Poly(oxy - 1,2 - ethanediyl), .α- (9Z) - 1 - oxo - 9 - octadecen - 1 - yl -ω- (9Z) - 1 - oxo - 9 - octadecen - 1 - yl oxy - (Polyethylene Glycol Dioleate) Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) *derivs*. (Polysorbate 85)

	Alkanes, C14-30

Table 1. Approved Oil Dispersant Products and Their Ingredients (con't)

DISPERSIT SPC 1000 (U.S. Polychemical Corp.)	Poly(oxy - 1,2 - ethanediyl), α- (9Z)- 1 - oxo - 9 - octadecen - 1 - yl - ω- hydroxyl Ethoxylated Amines, tallow alkyl N,N-bis(hydroxyethyl)- Amides, coco **Ethoxylated Alcohols, C_{12}-$_{14}$-secondary,** 1(or 2) - (2-methoxymethylethoxy) - propanol
SAF-RON Gold (Sustainable Environmental Technologies, Inc.)	Proprietary
NEOS AB3000 (Neos Company, Ltd.)	Proprietary
SEA BRAT 4 (Alabaster Corp.)	Proprietary

Table 2. Acute Toxicity of 2-Butoxyethanol (2-BE) and Dipropylene Glycol n-*t*-Butyl Ether (DPnB) in Various Species and Routes of Exposure

Route of Administration	Species Tested	LC_{50} or LD_{50}
Inhalation		
2-BE	Male rats (4 hr)	486 ppm (2347 mg/m^3)
	Female rats (4 hr)	450 ppm (2174 mg/m^3)
	Mice (7 hrs)	700 ppm (3381 mg/m^3)
	Guinea Pigs (1 hr)	650ppm (3140 mg/m^3)
DPnB	Rats (4 hr)	> 42 ppm (> 328 mg/m^3) (no deaths)
	Rats (4 hr)	> 262 ppm (> 2,040 mg/m^3) (no deaths)
Oral		
2-BE	Rats	2500 mg/kg b.w.
	Mice	1400mg/kg b.w.
	Guinea Pigs	1200 mg/kg b.w.
	Rabbits	320 mg/kg b.w.
DPnB	Rats	4000 mg/kg
	Rats	1850 mg/kg
	Mice	2160 mg/kg
Dermal		
2-BE	Rabbits	404-502 mg/kg b.w.
	Guinea Pigs	2000 mg/kg b.w.
DPnB	Rat	> 2000 mg/kg (no deaths)

(length of exposure)

The Future of Dispersant Use in Spill Response

NOAA Disaster Response Center
Held at the Greater Gulf State/Mobile Fairgrounds
Mobile, Alabama • September 20-22, 2011

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The Future of Dispersant Use in Spill Response

NOAA Disaster Response Center
Held at the Greater Gulf State/Mobile Fairgrounds
Mobile, Alabama

September 20-22, 2011

TUESDAY, SEPTEMBER 20

8:30 AM **Registration/Check-In**

9:00 AM **Welcome -** Nancy Kinner, *UNH Co-Director, Coastal Response Research Center*
Charlie Henry, *NOAA Gulf of Mexico Disaster Response Center*

9:10 AM **Background & Workshop Goals/Outcomes -** Doug Helton, *NOAA OR&R*

9:25 AM **Introductions of Participants -** Nancy Kinner

10:00 AM **Opening Remarks -** Doug Helton
Robert Pond, *U.S. Coast Guard*
(TBA), *U.S. EPA*
Ryan Gottschall, *U.S. Government Accountability Office*

10:20 AM **Workshop Structure & Logistics** - Nancy Kinner

10:30 AM **Setting the Stage: Dispersant Use During DWH** - Charles Huber, *C.A.Huber, Inc*
Charlie Henry, *NOAA OR&R*

11:00 AM **BREAK**

11:15 AM **Mini-topic Presentation** (5 min talk / 5 min questions)
White Paper Authors
1. Dispersant Efficacy and Effectiveness (*Thomas Coolbaugh, Amy McElroy*)
2. Physical Transport/Chemical Behavior of Dispersants/Dispersed Oil (*CJ Beegle-Krause, James Payne*)
3. Degradation of Dispersants and Dispersed Oil (*Kenneth Lee, Brian Wrenn*)
4. Biological Effects of Dispersants/Dispersed Oil (*Adriana Bejarano, Sara Edge, Ronald Tjeerdema*)
5. Dispersants and Seafood Safety (*Robert Dickey, Walton Dickhoff)*
6. Dispersants and Human Health (*James Fabisiak, Bernard Goldstein*)
7. Dispersants and Risk Communication (*Ed Levine, J. Steven Picou*)
8. Chemical Analysis of the Dispersant Corexit 9500 (*Irv Schultz, Jeff Ward)*

12:45 PM **LUNCH**

1:15 PM **Breakout Session I: Review of White Papers**
1. Discuss significant omissions (data, references, topics, current knowledge).
   Discuss whether irrelevant information is included.
2. Review the R&D needs presented in the white paper.

3:00 PM **Group Reports** (10 minutes each)

5:15 PM **Adjourn**

6:30 PM **Group Dinner—all participants** (Felix FishCamp Grill)

WEDNESDAY, SEPTEMBER 21

8:30 AM **Continental Breakfast**

9:00 AM **Overview and Review**

9:10 AM **Breakout Session II: Decision Makers Perspective**
1. What information do decision makers need to know to address the possible uses of dispersants in future spills?
2. Is this information available? If not, what R&D needs will fill the gaps?

12:00 PM **Lunch**

1:00 PM **Breakout Session III: Prioritize R&D Needs**
1. Fill out template for each R&D need discussed in previous two breakout sessions. (i.e., Session 1 & 2—included in white paper and to fulfill decision maker needs)
2. Prioritize the R&D needs. (from highest #1 to lowest priority)

4:00 PM **Group Reports**

5:15 PM **Adjourn**

Dinner (on your own)

THURSDAY, SEPTEMBER 22

8:30 AM **Continental Breakfast**

9:00 AM **Plenary Session: Synthesis and Next Steps**

11:30 AM **Closing Remarks**

Dispersant Efficacy and Effectiveness

Breakout Session 1: Review White Papers

(1) Discuss significant omissions (data, references, topics, and current knowledge). Discuss whether irrelevant information is included?

Omissions:	Type: (data, reference, topic, current knowledge)
Impossible to disconnect from biological effects	
Balance what we do know with what we don't know	
Effectiveness of different application techniques (subsea and surface)- comparisons	
Field evaluation techniques (disappearance of oil from surface, no way to directly measure)	
Definition of effective- performance based vs. science based (interfacial tension)	
Difference between performance and effectiveness	
History of effectiveness test results (selection criteria)	
Different spills warrant different responses and different dispersants	
Measures for effectiveness surface/subsurface e.g. thermal, particle size, fluorescence	
Challenge of real time subsea measurements	
Stockpiling multiple products for different scenarios	
New formulations and application rates as related to toxicity	
Environmental concentrations of dispersants	
Regulations for application subsea (height above sea floor)	
Using less of a more toxic formula vs more of a less toxic formula	
Explanation of the range of dispersed oil percentages	
Base line is an environment contaminated by an oil spill. Not a oil free environment	
Effectiveness of dispersant at 40% or 80% leads to similar risk levels for sensitive parties	
Reduce uncertainty. Don't need to answer every question. Stress the positives/knowns	
Show certainty levels of negative effects from inaction.	
Focus is not on trade off between introducing oil into the water column with dispersants and dealing with it on the surface or shore	
How much wave/mixing energy is necessary?	
Expand understanding of the operability window of dispersant use in general	
Key parameters- turbulence, viscosity	
Dispersant use in cold environments/ice	
Physically dispersed vs chemically dispersed	

Irrelevant information: (list below)

- Biological fate and effects of “Green” dispersants
- Risk communications

Review the R&D needs presented in the white paper. (list below)

- Extrapolation to environmental conditions (operational result)
- Mechanism of delivery (best effect with minimal dispersant)
- Subsea delivery system (besides just the wand)
- Specific subsea dispersant (solvent-less)
- Is there a reason to have two different types of dispersants
- Effectiveness monitoring immediately and over time (surface and subsurface), Mass Balance
- Controlled field studies in the U.S. to allow quality data acquisition
- Development of effective “Green” dispersants
- Viscosity/slick thickness thresholds for dispersant application
- Observation and targeting of target application areas (without confusing mud and seaweed)
- Oil behavior at extreme depth without dispersant

Breakout Session 2: Decision Makers Perspective
(use table below to record discussion of both questions)

1. What information do decision makers need to know to address the possible uses of dispersants in future spills? Was this addressed in the white paper?

2. Is this information available? If not, what R&D needs will fill the gaps?

Decision maker info need	**Info available? (Y or N)**	**In white paper? (Y or N)**	**R&D Need**
Do dispersants work on this type of oil in these conditions, and in concert with other techniques i.e. burning etc.	Y-surface N-subsea Maybe additional info required	Y-surface N-subsea Maybe additional info required	-Subsurface efficiency, oil type and characteristics, energy state (high speed turbulent jet vs. seep) -Develop real time monitoring (ROV etc.) -Quantitative measures for effectiveness
Will they be used			N/A
What's the best to use	Y- Selection guide (incomplete)		-Subsea/cold water testing -Product Schedule (sub part J)
What's available	Y		-Product Schedule (sub part J), realistic production capability (stockpiles) -Evaluate other dispersants not on EPA schedule
Difference between surface and subsurface application	Y- addressed above		
Coordination with stakeholders and resource managers			Need for continued R&D based discussion amongst stakeholders e.g. ICCOPR
What are the good and bad effects of dispersants (trade-offs)			N/A- Primarily biological fate and effects
Updated information during a response in real-time	N		-Instrumentation for monitoring effectiveness
Information formatted in useful ways	Not really		-Universal information management systems (spec document)—bottom up approach -Tend to be user and topic specific
Effectiveness monitoring to validate decisions e.g. SMART			
Confidence that response is still working			
Long-term monitoring vs. activities during the response			
Identification of a near-term actionable result			

Operational depth ranges for dispersants	N		-All subsea -Pressure, Temperature, Flow rate, Delivery Systems
What’s the difference between dispersing and not dispersing	See above (trade-offs)		
Field trials of different dispersants (Spill of Opportunity)	N		
Oil:Dispersant ratio (surface vs. subsea)	Y-surface N-subsea		
What are the tools for monitoring effective dispersion in the water column (surface and subsea)			
Continuous vs. Single release decision rules	Y-single N-continuous		-Currently under discussion by agencies (NRT)
Dispersant use combined with long-term monitoring			
On scene monitoring with ROV’s (subsea and air)			
Are subsea application techniques functional at 5000ft, 7500ft, 10000ft	See above		
Good flow rate estimates (amount of oil spilled), and composition of oil	N		-type of spill dependant (single vs. continuous) -Requirement of a science based estimate

Breakout Session 3: Prioritize R&D Needs

1. Fill out template for each R&D need discussed in previous two breakout sessions. (i.e., Session 1 & 2 – included in white paper and to fulfill decision makers needs)
2. Prioritize the R&D needs. (from highest #1 to lowest priority)

Template:

Research Topic	**Subsea dispersant effectiveness**
Objectives	Define the conditions of operability for dispersant use -What to apply? (dispersant characteristics) -When to apply? (physical parameters) -How to apply? (flow rate, mechanism, DOR) -How effective will it be? (type of oil, characteristics of source) -Confirm VOC reduction for worker safety. (Potential H&S project)
Guidelines (including whether lab/field study, etc)	-Coordination with other ongoing R&D efforts -lab→meso-scale→field
Issues/Problems	-Wide range of potential release conditions to be considered -Volume, Pressure, Depth, oil characteristics etc. -Specialized facilities required for deep sea conditions
Application to decision making process	-Efficiency of response -Identification of trade-offs -Reduction of uncertainty -Identifying technology and equipment gaps -Worker safety benefits from reduced VOC exposure
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	>2 yr
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	High

Research Topic	**Innovative analytical techniques for surface and subsurface**
Objectives	-Improve aerial surveillance for identifying thick oil (surface) -Improve targeting of thick oil (surface) -Improve instrumentation for measuring dispersant effectiveness e.g. ROV’s (subsea and surface) -Availability of information during response in real-time -Refine “SMART” protocol for subsea and surface response
Guidelines (including whether lab/field study, etc)	-Coordination with other ongoing R&D efforts -lab→meso-scale→field
Issues/Problems	-testing a wide range of technologies -inherent limitations of specific technologies -scalability from lab to field -Permits for field studies
Application to decision making process	- improves operational effectiveness -supports decision making process of continued use
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	>2
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	High

Research Topic	**New dispersants**
Objectives	-Develop new highly effective dispersants for use in different extreme environments -Evaluate need for separate subsea specific dispersant
Guidelines (including whether lab/field study, etc)	-Depth, pressure, temperature, ice -consider the use of environmentally benign materials
Issues/Problems	-Getting large scale production -scalability from lab to field -Permits for field studies
Application to decision making process	-Address stakeholder concerns about existing approved products
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	>2
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	High

Degradation of Dispersants and Dispersed Oil

Breakout Session 1: Review of White Papers

1. Discuss significant omissions (data, references, topics). Discuss whether irrelevant information is included?

Omissions (data, references, topics):	Irrelevant Information:
-How dispersants affect microbial processes (e.g., nutrient cycling, contaminant transformation) -Influence of nutrient availability on oil biodegradation at sea -How dispersants affect co-metabolism -Translation of what we've learned in the gulf to other areas (e.g., the arctic) specifically looking at temperature and microbial communities -How do we conduct experiments under conditions which we find in the environment? (Temp., nutrient, salinity, UV light, concentrations of oil and bacteria)	

2. <u>Review the R&D needs presented in the white paper.</u>
   <u>(List R&D needs below)</u>

- What's the difference in degradation rates between chemically and physically dispersed oil (surface vs. shoreline vs. water column)
- Need for more direct experimental studies BCF/BAF of individual Corexit components
- Analyses of individual components of surfactants at realistic concentrations
- In situ bug traps (developed at the U. of Tulsa) as well as chemical traps, much better due to limitations in the lab
- Study biodegradation of oil from deep sea dispersant injection
- Affects of gas components on oil biodegradation

Breakout Session 2: Decision Makers Perspective
(use table below to record discussion of both questions)

1. What information do decision makers need to know to address the possible uses of dispersants in future spills? Was this addressed in the white paper?
    - Does dispersant use for this specific incident provides net environmental benefit over non-use?
    - What limitations for dispersant use should be considered? (Duration of application, water depth applied, application location, type of oil, type of dispersant, windows of application opportunity, species of concern)
    - I need an operational monitoring program to verify that dispersant is working and that it is enhancing natural dispersion and to provide an operational endpoint.
    - What is the fate of the oil? Will the dispersed oil plume remain suspended in the water column and does not resurface, re-coalesce, or drift down and mix with the sediments.
    - Verification that the dispersant and chemically dispersed oil droplets are being biodegraded. What is the rate of biodegradation, extent of biodegradation in relation to naturally dispersed and undispersed oil.
    - What are the other degradation mechanisms in addition to biological?
    - What are the acute and chronic impacts on surface, water column, and benthic communities
    - How does sub-sea dispersant application affect VOCs on the surface?

2. Is this information available? If not, what R&D needs will fill the gaps?

Decision maker info need	Info available?	In white paper? (Y	R&D Need

	(Y or N)	or N)	
Does dispersant use for this specific incident provides net environmental benefit over non-use?	N/A	N/A	Integrated decision support tool to evaluate impacts on the system as a whole.
What limitations for dispersant use should be considered? (Duration of application, water depth applied, application location, type of oil, type of dispersant, windows of application opportunity, species of concern)	N/A	N/A	Information on persistence of dispersants (all listed products) in open water.
I need an operational monitoring program to verify that dispersant is working and that it is enhancing natural dispersion and to provide an operational endpoint.	N/A	N/A	
What is the long term fate of the oil? Will the dispersed oil plume remain suspended in the water column and does not resurface, re-coalesce, or drift down and mix with the sediments.	Some	Some	*Research on more oil types and environmental conditions. Development of standard testing protocols. Integration of biodegradation rates to predictive models.*
Verification that the dispersant and chemically dispersed	Some	Yes	*Need field experiments (changes in microbial community structure and function, fluorescence, stable isotope*

oil droplets are being biodegraded. What is the rate of biodegradation, extent of biodegradation in relation to naturally dispersed and undispersed oil.			*analysis).* *Development and application of tools including models that provide multiple lines of supporting evidence during actual spill events (analytical tracers).*
What are the other degradation mechanisms in addition to biological?	Some	Some	*Determine the significance of photo-degradation, other weathering processes in the presence of dispersants.* *Interaction between chemically dispersed oil and suspended material (SPM).*
What are the acute and chronic impacts on surface, water column, and benthic communities	N/A	N/A	
How does sub-sea dispersant application affect human safety and health (VOCS, LELs, etc) on the surface?	Some	Yes	Needs additional field and lab research. Some supporting data available from DWH that can be reevaluated.

Breakout Session 3: Prioritize R&D Needs

DEGRADATION BREAKOUT GROUP:

The Research Project	Degradation rates of dispersed oil
Objectives	A *research program* on quantification of degradation rates of chemically dispersed, physically dispersed, and undispersed oil.
Guidelines (including whether lab/field study, etc)	1. Compare oil degradation on surface vs. shoreline vs. water column vs. sediment 2. Develop analytical protocols for detection of chemical dispersants and degradation rates under variable environmental conditions 3. Develop the ability to conduct "science of opportunity" from unanticipated spills, R&D response team 4. Need field experiments (changes in microbial community structure and function, fluorescence, stable isotope analysis) 5. Influence of suspended particulate material on dispersed oil degradation 6. Development and application of tools including models that provide multiple lines of supporting evidence during actual spill events (analytical tracers) 7. Determine the significance of photo-degradation, other weathering processes in the presence of dispersants 8. Integration of biodegradation rates to predictive models 9. Study biodegradation of oil from deep sea dispersant injection
Issues/Problems/ Opportunity	Expensive, requires a well coordinated, multi-disciplinary effort. Needs to be coordinated with other R & D efforts on issues like fate and transport, modeling, biological effects, etc; National funding programs such as ESTCP and SERDP may be funding sources
Application to decision making process	***Provides critical information related to oil degradation required for the development of operational guidelines.***
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	>5 years Key milestones and deliverables all along the way.
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	High. Looking at 9 individual projects each funded in the medium-high range. Expectation that these projects will be leveraged with other funding and national user facilities.

DEGRADATION BREAKOUT GROUP:

Research Project 2	Effect of sub-sea dispersant application on water soluble hydrocarbons

Objectives	Impact of chemical dispersants on the dissolution/degradation of water soluble hydrocarbons including VOCs from subsea releases
Guidelines (including whether lab/field study, etc)	• Reevaluation of existing DWH data • Lab experiments to fill data gaps • Design a study plan for either spill of opportunity or controlled experimental spill
Issues/Problems	Spills of opportunity only represent a specific situation. Human health concerns.
Application to decision making process	Supports FOSC decision to apply dispersants to protect human health.
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	1-2 years (potential for 1 year)
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	Medium

Physical Transport/Chemical Behavior of Dispersed Oil

1. Discuss significant omissions (data, references, topics). Discuss whether irrelevant information is included?

Omissions (data, references, topics):	Irrelevant Information:
- Dispersion effected by temperature, outlet pressure (phase equilibrium critical) - Current oil droplet size and distribution research at SINTEF using tower basins - Research using holographic cameras to send out a laser pulse to measure diffraction off of oil droplets, can detect particle size - What size is a "small" oil droplet - How does dispersant use affect dissolution as oil particles rise to the surface? - No reference of hydrate formation - Gas bubble distribution influenced by dispersant use - Dispersant injection methods and effectiveness - Look at different kinds of dispersants optimized for subsurface use	- References to biodegradation

2. **Review the R&D needs presented in the white paper.**

(List R&D needs below)

- How long does surfactant stay with dispersed oil particles?
  - Wave tank tests (Exxon-Mobil)
- Look back at Macondo for chemistry data, photographic evidence
  - Time series of dispersant injection

1. R&D Need: How do we measure critical parameters at the surface given the operating constraints?

2. R&D Need: How do we measure critical parameters at the wellhead given the operating constraints?
3. R&D Need: determine the minimum depth at which dispersants should not be used
4. R&D Need: Is there any case where you should not use dispersants in the subsurface (shallow and deep)?
5. R&D Need: Is there any case where you should not use dispersants at the surface?
6. R&D Need: Integrating microbial degradation and dissolution information into contingency planning
7. R&D Need: deep water dispersion of soluble components
8. R&D Need: local tools on mixed layer dynamics for particular regions
9. R&D Need: consolidate models and tools to provide a listing of available resources that decision makers have access to
10. R&D Need: Extending ESI maps into subsurface
11. R&D Need: box model of concentrations of oil in the water column
12. R&D Need: decision support tools that include information regarding regional conditions and specific local species over entire life histories
13. R&D Need: Using dispersants on sinking oils
14. R&D Need: making the physical transport and biological information coordinate
15. Recommendation: put tools for analyzing the effects of dispersants in contingency plans accessible to the public domain
16. Recommendation: money be set aside to cover expenses for modelers and local decision makers to attend workshops in different regions
17. R&D Need: Local modeling
18. R&D: Timing of dispersant application
19. R&D Need: at what sediment/microbial load does oil become neutrally buoyant or more dense than seawater?
20. R&D Need: long term weathering to be more informed about dissolution
21. R&D Need: Look back at Macondo for chemistry data, photographic evidence (data mining)
22. R&D Need: How long does surfactant stay with dispersed oil particles?
23. Could a frictional/mechanical oil droplet dispersion method be more effective at creating smaller droplets than the subsurface application of chemical dispersant?
24. How effective is application of subsurface dispersant in creating more small droplets? What specific dispersant injection methods (and/or orientations relative to the plume) are necessary to accomplish various degrees of effectiveness?
25. Can subsurface injection of chemical dispersant reliably reduce the amount of oil reaching the surface?
26. How would we better measure subsurface chemical dispersant effectiveness during the next event?
27. How do these processes affect biodegradation kinetics, composition of sedimented oil, and the ultimate fate of dispersed oil?
28. Can SMART Protocol improvements be developed to allow better tracking of dispersed oil at depth?
29. Literature synthesis on physical and chemical properties of oils that determine the overall effectiveness of dispersant application (largely completed);

30. Refining existing datasets to correlate physical and chemical properties of different types of oil with dispersability (ongoing);
31. Update SMART monitoring protocols;
32. Workshop on requirements for integrating oil toxicity and biological data with oil fate and transport models;
33. Improved models to predict dispersant effectiveness and oil fate;
34. Understanding the interactions of chemically dispersed oil droplets with suspended particulate matter (largely completed) and how these processes affect the rate of oil biodegradation and ultimate fate of dispersed oil (ongoing);
35. Assessment of the degree, rate, and consequences of surfactant leaching from surface slicks and chemically dispersed oil droplets;
36. Reconciliation of the differences between the empirical evaporation approach and traditional pseudo-component approach;
37. Improve, verify, and validate oil-spill trajectory and fate models;
38. Monitoring dispersed oil concentrations at spills of opportunity; and
39. Integration of fate and toxicity models with population models to predict short- and long-term effects of dispersant application.
40. We need to transition our understanding of surface dispersant application and effectiveness to the specific case of a deepwater well blowout. Topics/data needs include:
    a. Evaluation of our understanding of the mechanism of dispersed oil droplet shearing and droplet fractionation under subsurface conditions.
    b. Evaluation of emulsion stability for surface oils previously weathered by dissolution (e.g. surface oil slicks created from droplets rising from a deepwater well blowout) with and without the application of subsurface chemical dispersants.
41. What methods and protocols could be used to determine effectiveness of subsurface chemical dispersant application for decision support? Topics/data needs include:
    a. Measurements to support detailed water mass analysis of oceanographic and oil spill related chemical parameters,
    b. Measurements of mixing energy, target or actual dispersant-oil-ratios (DOR), the duration of oil-dispersant interactions,
    c. Measurement of the effectiveness of dispersants as a function of plume characteristics
    d. Measurements of dispersant components within oil droplets (as isolated from the dissolved phase by the Portable Large Volume Water Sampling System (Payne *et al.*, 1999),
    e. Measurements of droplet size distribution and temporal variance,
    f. Near-real-time measurement systems that can work near a deepwater blowout well without interfering with response activities or near-real-time proxies that can be measured outside the response exclusion zone.
    g. Quantitative near-real-time evaluation of the footprint (x,y,t), mass(t) and chemical composition (x,y,t) of the freshest surfacing oil.
42. What is the role of physical scavenging (oil/SPM interactions) in chemical dispersant application and effectiveness (surface and subsurface)? Topics/data needs include:

    a. Spatial and temporal (*x*,*y*,*z*,*t*) background, natural variance, and near-real-time SPM concentrations (number density or particle sizes) in the water column,
    b. Near-real-time measurement systems that can work near a deepwater blowout well without interfering with response activities or near-real-time proxies that can be measured outside the response exclusion zone,
    c. Protocols for decision support evaluation of mucus agglomerates for chemical signatures of dispersants or byproducts of biological interaction with dispersant components or dispersed oil droplets,
    d. Protocols for decision support sediment core analyses near the wellhead (<2-4 *km*) in the upper sediment layers (0-1 *cm*) for evidence of dispersant effects, e.g. oil/SPM interactions, flocculation, and sedimentation, fecal pellets containing dispersant products, and other response related chemical constituents (e.g. drilling mud),
    e. Detailed analysis of SPM interactions with oil droplets, and
    f. How these processes affect biodegradation kinetics, composition of sedimented oil, and the ultimate fate of dispersed oil.

43. Are the effects of photolysis the same on chemically- and physically-dispersed oil droplets?
44. Prepare post DWH guidance documents for:
    a. Decision makers on effects of chemically dispersed oil,
    b. The scientific community on oil-related sampling equipment, standard analyses, and fingerprinting.

Mining data from DWH [21]

Is there a correlation between the surface expression of oil and dispersant application?

Does this provide quantitative information on subsurface dispersant effectiveness when compared to the application time series?

Is all evidence of emulsified oil at the surface evidence of oil that was not successfully treated at the subsurface?

Subsurface Observations

How do we measure and observe oil droplet size and distribution

Need for data at the source (near field)

How do we measure critical parameters at the wellhead given the operating constraints?

[26] How would we better measure subsurface chemical dispersant effectiveness during the next event?

Need for data at far field

[28] Can SMART Protocol improvements be developed to allow better tracking of dispersed oil at depth?

[41b,c,e] What methods and protocols could be used to determine effectiveness of subsurface chemical dispersant application for decision support? Topics/data needs include: Measurement of the effectiveness of dispersants as a function of near field/far field plume characteristics (Measurements of mixing energy, target or actual dispersant-oil-ratios (DOR), the duration of oil-dispersant interactions; Measurements of droplet size distribution and temporal variance)

Surface Observations

Oil Droplet Size and Distribution in the field

Need for data at far field

[1] How do we measure critical parameters at the surface given the operating constraints?

[31] Update SMART monitoring protocols (See California DOMP)

Modeling and Predictive Ability

Mixed layer models

[3,4,5] Planning and Resource Management

[9] Need for a list of localized tools available to local planners/responders, and where they can be found

[10] Extending ESI maps to subsurface and open water

[12,18] Decision support tools that include information regarding regional oceanographic conditions and specific local species over entire life histories, including important life events (timing)

[14,39] Making the physical transport and biological information coordinate (matching models), workshop? Integration of fate and toxicity models with population models to predict short- and long-term effects of dispersant application

[36] Reconciliation of the differences between the empirical evaporation approach and traditional pseudo-component approach

[29,30,33] Literature synthesis on physical and chemical properties of oils that determine the overall effectiveness of dispersant application (largely completed); Refining existing datasets to correlate physical and chemical properties of different types of oil with dispersability (ongoing); Improved models to predict dispersant effectiveness and oil fate

[40a] We need to transition our understanding of surface dispersant application and effectiveness to the specific case of a deepwater well blowout. Topics/data needs include: Evaluation of our understanding of the mechanism of dispersed oil droplet shearing and droplet fractionation under subsurface conditions.

[42] What is the role of physical scavenging (oil/SPM interactions) in chemical dispersant application and effectiveness (surface and subsurface)?

Data Gaps

[19] R&D Need: at what microbial load does oil become neutrally buoyant or denser than seawater?

Chemistry

Thermodynamics and Kinetics of Dispersants

[22] R&D Need: How long does surfactant stay with dispersed oil particles?

[27] How do these processes affect biodegradation kinetics, composition of sedimented oil, and the ultimate fate of dispersed oil?

[34] Understanding the interactions of chemically dispersed oil droplets with suspended particulate matter (largely completed) and how these processes affect the rate of oil biodegradation and ultimate fate of dispersed oil (ongoing)

[35] Assessment of the degree, rate, and consequences of surfactant leaching from surface slicks and chemically dispersed oil droplets

[7] Role of dispersant on the dissolution process

[20] R&D Need: long term weathering to be more informed about dissolution

[40b] Evaluation of emulsion stability for surface oils previously weathered by dissolution (e.g. surface oil slicks created from droplets rising from a deepwater well blowout) with and without the application of subsurface chemical dispersants.

[43] Are the effects of photolysis the same on chemically- and physically-dispersed oil droplets?

Physical Transport and Chemical Behavior of Dispersed Oil

Addendum to Notes

Research Needs from the Fate and Transport Group – UNH CRRC Workshop "The Future of Dispersant Use in Spill Response", September 20-22, 2011, Mobile, Alabama

The Workshop Fate and Transport Group (CJ Beegle-Krause, Michel Boufadel, Cortis Cooper, Margaret Childs, Robyn Conmy, Per Daling, Steve Gittings, Ginger McMullin, Eric Miller, James Payne, Kalliat Valsarj, Marieke Zeinstra) developed a listing of research needs. The list below, based on notes compiled at the workshop and organized to enhance readability, reflects the summarized opinions of the members of the group.

Mining data from DWH

- Is there a correlation between the surface expression of oil and dispersant application time series?
    - Does this provide quantitative information on subsurface dispersant effectiveness when compared to the application time series?
    - Is all evidence of emulsified oil at the surface evidence of oil that was not successfully treated at the subsurface?
- Why was mousse formation only observed at distances greater than 5-10 *km* from the well? Was it because the oil had to go through photo-oxidation and further weathering before emulsifying?
- What other DWH observations could be used to quantify any efficacy of subsurface dispersant application?

Subsurface Observations

- Need for data at the source (near field):
    - How do we measure critical parameters at the wellhead given the operating constraints?
    - How would we better measure subsurface chemical dispersant effectiveness during the next event?
- Need for data at far field distances (>10 *km*) from the well location.
- How do we measure and observe oil droplet size and distribution?
- Can SMART (Special Monitoring of Applied Response Technologies) Protocol improvements be developed to allow better tracking of dispersed oil at depth?
    - Include protocols for monitoring of surface oil physical properties (*e.g.* emulsion thickness, viscosity, water content, field-tested dispersibility) prior to dispersant spraying and on eventual remaining oil/emulsion after treatment.
- What methods and protocols could be used to determine effectiveness of subsurface chemical dispersant application for decision support? Topics/data needs include:
    - Measurement of the effectiveness of dispersants as a function of near field and far field plume characteristics, such as measurements of

        - mixing energy,
        - target and/or actual dispersant-oil-ratios (DOR),
        - duration of oil-dispersant interactions;
    - Measurements of droplet size distribution and its temporal variance.

Surface Observations

- Oil droplet size and size distribution in the field
    - Need for data at far field distances from the well location,
    - What is the compressibility of oil, particularly as compared to water at high pressure (deep ocean depths)?
- How do we measure critical parameters at the surface given the operating constraints?
- Update SMART monitoring protocols (See California Dispersed Oil Monitoring Plan (DOMP))

Modeling and Predictive Ability

- Planning and Resource Management
    - Need for a list of localized tools (with sources) available to local planners and responders,
    - Extend ESI maps to subsurface and open water,
    - How should flushing rates be considered in guidance for shallow water dispersant operations?
    - Decision support tools that include information regarding:
        - regional oceanographic conditions, particularly mixed layer dynamics and variability, and
        - key local species information over their entire life histories, including important life events (timing).
    - What information, particularly biological, can be leveraged from the field studies previously done in Panama and Maine, U.S., related to long-term biological effects of oil and chemical dispersants.
- Integrated Physical/Biological models
    - Workshop on coordinating (matching) the physical transport and biological information,
    - Integration of fate and toxicity models with population models to predict short- and long-term effects of dispersant application.
- Reconciliation of the differences between the empirical evaporation approach and traditional pseudo-component approach.
- Literature synthesis on physical and chemical properties of oils that determine the overall effectiveness of dispersant application (largely completed).
- Refining existing datasets to correlate physical and chemical properties of different oil types with dispersability (ongoing).
- Improved models to predict dispersant effectiveness and oil fate.
- We need to transition our understanding of surface dispersant application and effectiveness to the specific case of a deepwater well blowout. Topics/data needs include:

    - Evaluation of our understanding of the mechanism of dispersed oil droplet shearing and droplet fractionation under subsurface conditions.
- What is the role of physical scavenging (oil/SPM interactions) in chemical dispersant application and effectiveness (surface and subsurface)?

Data Gaps

- At what microbial load does oil become neutrally buoyant or denser than seawater?
- Can subsurface dispersant application be used to respond to sinking oils?

Chemistry

- Thermodynamics and kinetics of dispersants
    - How long does surfactant stay with dispersed oil particles?
    - How do these processes affect biodegradation kinetics, composition of sedimented oil, and the ultimate fate of dispersed oil?
- Understanding the interactions of chemically dispersed oil droplets with suspended particulate matter (largely completed) and how these processes affect the rate of oil biodegradation and ultimate fate of dispersed oil (ongoing).
- Assessment of the degree, rate, and consequences of surfactant leaching from surface slicks and chemically dispersed oil droplets.
- Role of dispersant on the dissolution process.
- Long-term (weeks to months) weathering studies to be more informed about dissolution effects including changes in droplet diameter and buoyancy.
- Evaluation of emulsion stability for surface oils previously weathered by dissolution (e.g. surface oil slicks created from droplets rising from a deepwater well blowout) with and without the application of subsurface chemical dispersants.
- Are the effects of photolysis the same on chemically- and physically-dispersed oil droplets?

Biological Effects of Dispersants and Dispersed Oil

Breakout Session 1: Review White Papers

(1) Discuss significant omissions (data, references, topics, and current knowledge). Discuss whether irrelevant information is included?

Omissions:	Type: (data, reference, topic, current knowledge)
Refocus/ reorganize subsurface plume on page 11, around biology and ecology. Combine with fate and transport discussion (e.g. exposure pathways)	
Summary of operations and decision making actions- Applicable aspects for specific species or endpoints, model for high/moderate/low in compartmentalized species, for critical species or habitats/ priority of concerns (how can this be inferred from specific species, show how they can be connected, species sensitivity distribution [SSD's-for regions])	
Look at different exposure routes (e.g. coral), specific to different dispersants	
Separate oil versus dispersants versus dispersed oil effects	
What is the effect of dispersants on constituents already in sediments or other particulates (Indirect effects)?	
Effect of dispersant oil on hair, fur, feathers. Does it make harder to rehabilitate? Often found certain birds were not buoyant in water even without visual oil in place, not sure if dispersants were in these areas.	
Temperature changes effects	
Behavioral effects, even in very low concentrations from dispersants/ dispersed oil/oil, sub lethal (e.g. olfactory)	
Changes in route of exposure/bioavailability between oil/ dispersed oil, with respect to membrane across biotissue, filter feeders, transport, etc. Enhanced transfer into water, off particulates and sediments, changed from "natural" biodegradation, what is the background reference level	
Repeated exposures	
Tradeoffs	
Impacts to marine mammals repertory; inhalation and skin (whales dolphins)	
Review what is learned from other spills, not just DWH	
Effects on disease progression, susceptibility	
Look at broader range of dispersants look at all brands (not just Corexit)	

Irrelevant information: (list below)

- Content endorsed, non to remove

Review the R&D needs presented in the white paper. (list below)

Data Gaps noted by the White paper

- Photo-enhanced toxicity (fate and effect)
- Interactions of dispersed oil with sediment particles and its effects to benthic fauna
- Tests with representative/sensitive species at varying life stages
- Expanded species testing on dispersed oil effects, especially in inhibited biodegradation areas (e.g. low temperature)
- Delayed exposure effects
- Different exposure routes
- Toxicity from pathways other than narcosis (e.g. oxidative products, smothering)
- Long term effects on population and communities
- Inherent gaps in LC 50 tests (compare with much shorter, and rapidly diminishing exposures)
- Standardization with respect to dissolved vs. particulate oil phases, use of chemical signatures, etc.
- Consider temporal and spatial sampling intensity throughout spill duration to evaluate short and long-term effects to aquatic receptors
- Enhanced understanding of low temperature and high pressure on dispersed oil and dispersants, with respect to fate and effects in deep water
- What is the fate and effects of oil at depth if dispersant had not been applied directly to wellhead
- Correlation between oil droplet size distribution and oil constituent bioavailability and toxicity (dissolved vs. particulate oil)
- Increased sediment/toxicity sampling of deepwater bottoms
- Increased in-situ testing, as opposed to rotifer toxicity tests
- Photo-induced toxicity of chemically dispersed oil (at water surface)
- Expand toxicity sampling form PAH’s to other constituents (e.g. alkanes, isoparaffins, heterocycles, ect.)

- Environmental tradeoffs minimize impacts
  - Long-term effects
  - Population and recovery rate
- Pick driving species to see ecosystem affected, relevant to timing (Ecological niche, sensitive species, keystone species, cascading effect)
  - Define what makes a species sensitive, specific to each habitat

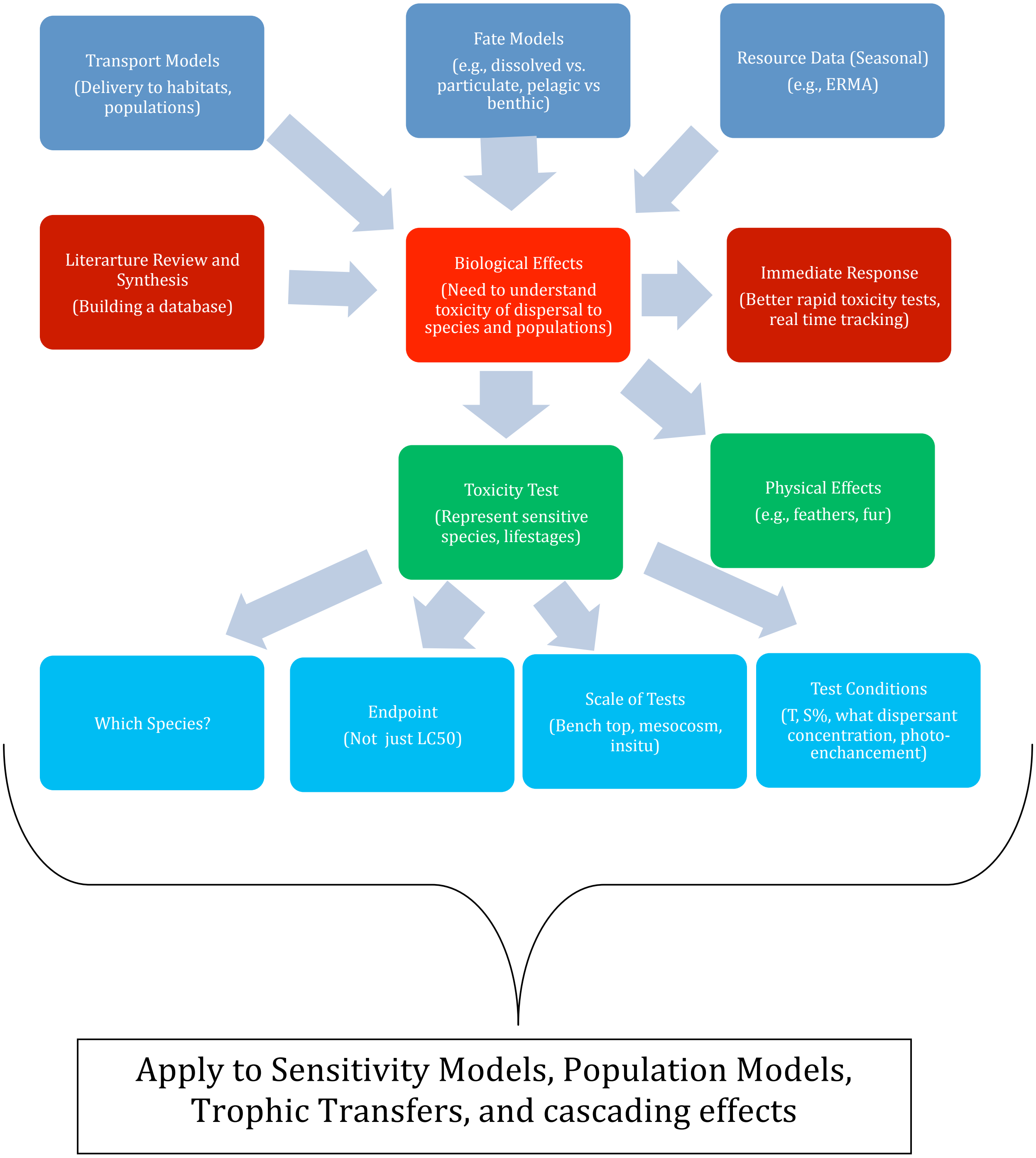
    - Specific sensitive areas
    - How to expand beyond specific areas/regions to generalization
- Generate benchmark toxicity data for specific species and life stages where existing data has highest unknown or uncertain extrapolations
    - Physical (e.g. Fur and feather) structure data lacking
    - Food, impair reproduction
- Address Great Lakes as part of responsible area, bring relevant data
- Regional population affects
- Population sensitivity ranking database for regional areas specific species of concern/ or resources at risk , and the exposure rate of concern, combine with fate and transport projection, and recovery time of population
- Layered GIS to model exactly what is relevant to the region, species of concern, long term
    - Habitat
    - Sensitivity
    - Etc.
- How to deal with “charismatic” species in terms of media relations vs. ecological benefits
- Population models for specific areas, not only species
- How are species actually being exposed to dissolved, particulate oil, sorbed to particulates, how does it affect the toxicology and recovery

Need biological effects data to build into database
Proxy specific species to cover as many as possible
Knowing resources present in ecosystem to establish baseline/ resources at risk
Pilot project on database and then do research to fill in specific gaps

Short term
Real time toxicity data- is it necessary for response?
Model where the spill is, and in what levels
Improve tracking, and what is the toxicity at certain times at sea?
Can we know all degradation products, and how will it be affected by different dispersants
Tox test in real time could tell when to no net environmental benefits would be made from applying more dispersants
Consistent approach on species for toxicity testing
Activated oil lab results not translating to real world lethal results

Database of lessons learned from past spills, open to public and decision makers categorize for responders

One year project to simplify all known data, and identify gaps, populate into database


Transport Models
(Delivery to habitats, populations)
Fate Models
(e.g., dissolved vs. particulate, pelagic vs benthic)
Resource Data (Seasonal)
(e.g., ERMA)
Literarture Review and Synthesis
(Building a database)
Biological Effects
(Need to understand toxicity of dispersal to species and populations)
Immediate Response
(Better rapid toxicity tests, real time tracking)
Toxicity Test
(Represent sensitive species, lifestages)
Physical Effects
(e.g., feathers, fur)
Which Species?
Endpoint
(Not just LC50)
Scale of Tests
(Bench top, mesocosm, insitu)
Test Conditions
(T, S%, what dispersant concentration, photo-enchancement)
Apply to Sensitivity Models, Population Models, Trophic Transfers, and cascading effects

Research Topic	Worldwide compilation, synthesis and analysis of biological effects from dispersed oil under controlled and uncontrolled oil spills
Objectives	1. Data mining of peer review and gray literature of worldwide information and dispersant use in field laboratory, and accidental oil spills 2. Evaluate and analyze available data in scientifically rigorous process to extrapolate to relevant situations or decisions 3. Easily accessible, summarized, searchable (keywords e.g. species, acute vs. chronic, characteristics), interactive and geo-referenced database on the effects of dispersant use 4. Initial report of findings with annual/ biannual updates
Guidelines (including whether lab/field study, etc)	Literature review of lab, field and real world monitoring
Issues/Problems	Accessibility for database (publicly accessible Maintenance and continuing updates (how, who, when, where) Training on database use (e.g. manual, on site trainings) Data may not be available (e.g. proprietary data
Application to decision making process	Informed tradeoff decisions based on past experiences Help identify risks and reduce uncertainty
Length of Time of Project (<1 yr; 1-2 yr; >2	2 years

yr)	
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	Medium (100,000 to 400,000)

Research Topic	Identifying Resources at Risk to Dispersed Oil: Population Sensitivity Analyses
Objectives	Create a Ecosystem Consequence Analysis (ECA) that considers key populations at risk, recovery rates, food web consequences, using

	Population Sensitivity Tables that inform many decisions (e.g., ecological to economic), identify data gaps, identify key species that drive tradeoff decisions
Guidelines (including whether lab/field study, etc)	Primarily a modeling approach. Use existing data to develop sensitivity tables and effects models
Issues/Problems	Lack of data to make resource-based decisions. Understanding of long-term impacts
Application to decision making process	Use of dispersants based on ecosystem consequences and tradeoffs.
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	2-3 yrs
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	300,000- 400,000

Research Topic	Developing a systematic process for area specific biological effects assessments for dispersant use: Application to two contrasting environments (Cook Inlet, Alaska and Florida Keys, Florida)
Objectives	1. Expand ERA process (transport, fate, receptors) to identify data gaps for determining area-specific biological effects

	of dispersed oil. Identify whether appropriate toxicity data and test conditions exists for resources at risk or their surrogates 2. Fill data gaps (additional information on transport, fate, resources, toxicity testing) to be able to apply results to decision making (including population models, trophic cascading effects). 3. Experimental validation at appropriate scales
Guidelines (including whether lab/field study, etc)	
Issues/Problems	Could not separate biological effects gap analysis from transport, fate, resources at risk Every region has differing transport, fate, resources at risk
Application to decision making process	Application to decision making process: Reduces uncertainty by providing relevant data
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	>2 years
Total Cost Estimate($) [High= >$400,000;	>400,000

Med =$100,000 – $400,000; Low = <$100,000]	

SEAFOOD SAFETY

Breakout Session 1: Review White Papers

(1) Discuss significant omissions (data, references, topics, and current knowledge). Discuss whether irrelevant information is included?

Omissions:	Type: (data, reference, topic, current knowledge)
White paper only covers Corexit products (focused on DWH dispersant use) -should develop similar discussion on other products -need systematic study of all dispersant formulas	
-more thoroughly describe the derivation of the ADI	
Nothing about sensory testing (esp. with respect to international spills – subsistence use and other issues with lack of resources and responsible party)	

Irrelevant information: (list below)

- NONE

Review the R&D needs presented in the white paper. (list below)

- More thorough study of products (all dispersant formulations) on seafood safety
  - Salinity, temperature, realistic exposure concentrations, exposure times,
  - Environmental toxicity (mortality) could be combined with studies (biological effects group)
  - Pathways of exposure (e.g., dermal, consumption)
  - Ideal metabolite
- Rapid method for screening for dispersant components in seafood samples
- Identify ideal chemical marker (alternative to DOS) for other dispersant formulas
- Go through same schedule as in FDA with Corexit for other dispersants on list
-

Breakout Session 2: Decision Makers Perspective

1. What information do decision makers need to know to address the possible uses of dispersants in future spills?
2. Is this information available
3. Was this addressed in the white paper?
4. If not, what R&D needs will fill the gaps?

Decision maker info need	Info available? (Y or N)	In white paper? (Y or N)	R&D Need
Have sensory, analytical and extraction methods avail that have the sensitivity and precision to accurately monitor conc	Avail for corexit, but not for others		• Extraction and analytical method for each dispersant • Establish minimum experiment design criteria wrt seafood safety (species, exposure times (e.g., CROSERF). • Identify appropriate chemical markers for different dispersants • Baseline environmental data for dispersant constituents, especially markers • Further development and validation of "electronic nose" • Better understanding of and validation of smell technique (i.e., what are you smelling, can all relevant compounds be detected) (must remember chemistry differences between oils preclude comparison between spills)
Accurate analytical stds for QA/QC	Yes		
Chemical makeup, kinetics, toxicity (mammalian), BCF/BAF, environmental concentrations and levels of concern. *(JC/ZM: interest in toxicity range/BCF/BAF will vary with species of interest and group seeking info)*	No (known for corexit, but not necessarily for others)		• Chemical Makeup • Kinetics • Toxicity • BCF/BAF • Environmental Concentrations and Levels of Concern

Structure and Size of fishery, consumption rates and dietary preferences, catch, demographics, ecology	May be regional differences in subsistence use and needs to be assimilated with avail info (e.g., arctic)		
Understanding of location and extent of major commercial fisheries and who would be impacted by closures/dispersant use. Impacts may diverse and global, must include risk and overall intake	Fairly well understood – including arctic regions		
Understanding of recreational fishery use	Well known overall		
Better understanding of who regulates what fishery (finfish, shellfish regulated by different groups)	While it is available, it takes time to pull together. ISSC may have the appropriate info		• Compilation of information, graphical depictions for unified command that are readily available and easily accessible.

Breakout Session 3: Prioritize R&D Needs

FINAL RANK

Final rank	
1	Conduct literature review of dispersant constituents that are found on the NCP product schedule to determine relevant information

	such as chemical makeup, environmental fate, kinetics, toxicity, BCF/BAF in order to identify constituents of concerns or chemical markers.
2	Establish standardized experiment design criteria and perform environmental fate, kinetics, BCF/BAF studies on constituents of concern
3	Establish standardized experiment design criteria and perform mammalian toxicity studies on constituents of concern in order to develop reference exposure levels.
4	Develop rapid extraction and analytical methods for each dispersant constituent of concern in seafood for response activities
5	Background dispersant constituent of concern levels in various species

Research Topic **Rank: #1**	Conduct literature review of dispersant constituents that are found on the NCP product schedule to determine relevant information such as chemical makeup, environmental fate, kinetics, toxicity, BCF/BAF in order to identify constituents of concerns or chemical markers.
Objectives	Identify available information and gaps
Guidelines (including whether lab/field study, etc)	Secondary research, literature review
Issues/Problems	Proprietary issues
Application to decision making process	Direct
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	< 1 year
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	Low

Research Topic **Rank: #2**	Establish standardized experimental design criteria and perform environmental fate, kinetics, BCF/BAF studies on constituents of concern
Objectives	To determine likelihood of exposure from seafood consumption
Guidelines (including whether lab/field study, etc)	Consensus based discussion; lab
Issues/Problems	Developing Consensus; time and money;
Application to decision making process	Critical to feed into decision making process
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	>2 years
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	High

Research Topic **Rank: #3**	Establish standardized experiment design criteria and perform mammalian toxicity studies on constituents of concern in order to develop reference exposure levels.
Objectives	Identify or Develop reference exposure levels
Guidelines (including whether lab/field study, etc)	Consensus based discussion; lab
Issues/Problems	Developing Consensus; time and money
Application to decision making process	Critical to feed into decision making process
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	>2 years
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	High

Research Topic Rank: #4	Develop rapid extraction and analytical methods for each dispersant constituent of concern in seafood for response activities
Objectives	To be able to quantify dispersant constituent of concern in a time-critical manner in a spill response
Guidelines (including whether lab/field study, etc)	Lab
Issues/Problems	Justification of selected constituent of concern
Application to decision making process	Yes
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	>2 years for multiple, < 6 months for individual
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	Medium for each individual constituent of concern

Research Topic Rank: #5	Surveillance of background dispersant constituent of concern levels in various species
Objectives	Determine background concentrations of constituents of concern in seafood
Guidelines (including whether lab/field study, etc)	Field sampling and lab analysis; time series
Issues/Problems	If pre-existing program is present will be easier (e.g., mussel watch, cruises of opportunity, EPA EMAP); regional differences
Application to decision making process	Yes
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	Individual < 1 year, but ongoing program
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	High (might be able to use pre-oiled samples as part of NRDA pre-exposure collection)

MISC NOTES

Discuss that the DOSS protocol based on JECFA used a different body weight assumption than was used for the PAH re-opening protocol. Important to be consistent moving forward for factors and assumptions

2,-3 ring PAHs odor thresholds are well known, heavier are less known

Criteria for closing fishery is observational – presence of oil and projections (due to time required to extract/analyze data).

Jurisdictional differences (state vs federal vs tribal) result in different closure/re-open criteria)

Public Communication: Better explanation of sampling, analysis, and statistical relevance to the public. Closer communication with states to help explain why sampling was done in one location vs another would be helpful.

Compilation of information, graphical depictions for unified command that are readily available and easily accessible.

Sensory and chemical analysis was done on all samples – but public perception is that sensory was only method used. Used routinely, and still a legal requirement in interstate commerce for tainting.

Formatting of output (reports) is different between agencies – may be helpful if they were similar

FDA conducted most of state seafood safety analysis, however individual states also analyzed samples, but FDA had a much higher throughput.

Suggest EPA standardize and enhance toxicity testing, chemical makeup, and identify any specific constituents that may be detectable by sensory techniques to provide risk input to responders to shift burden from responders to manufacturer

Clarification of Decision Maker: People who provide input on decision to use dispersants. Could also include decision to open/close fisheries. *Seafood Safety is much more unique than other groups and needs to be outlined in report – will interpret broadly (ZM/JC).*

Should remember that decision makers may include individuals – personal choices to limit or reduce seafood consumption.

Larval stages most sensitive to PAH and dispersant]

Better use of risk communication and understanding of hypersensitivity

Dispersants and Risk Communication

Breakout Session 1: Review White Papers
9/20/2011

(1) Discuss significant omissions (data, references, topics, and current knowledge). Discuss whether irrelevant information is included?

Omissions:	Type: (data, reference, topic, current knowledge)
Definition of Risk Communication	
Relationship with spill responders and reporters Needs to be improved	
Transparency explicit acknowledgment of spill response community limitations, with regard to institutional arrangements/legal requirements	
Enumerate stakeholder groups outside spill community(eg. Elected and appointed officials, fishermen, property owners etc.)	
Develop a plan to identify and engage with trusted intermediaries including public health community	

Additions : (list below)

- slide graphics
- Cite references for fair/not fair and contextual reporting eg. New Yorker article
- Reach out to thought leaders. Eg. Public health officials, ministers, trusted intermediaries
- What's the goal of oil spill risk communication?
    - Informed public
    - Explicit statement
- Internal and external information
- Develop a system which works in reality
- Unified command
- Paper pushed envelope to where risk communication needs to go for oil spill response, NOT just dispersants

Review the R&D needs presented in the white paper. (list below)

- Real time data and how to utilize data
- How to convey environmental tradeoffs
- Communication of shared values
- How to plan for and recognize human dimensions
- Acknowledge limitations of ICS structure to deal with political context

- Study reactions diverse stakeholders on DWH/other spills(cosco buscan) to identify opportunities for improved risk communications and potential strategies
- Development of participatory research action plans how to involve community before and during a response.
-

Breakout Session 2: Decision Makers Perspective
9/21/2011
(use table below to record discussion of both questions)

1. What information do decision makers need to know to address the possible uses of dispersants in future spills? Was this addressed in the white paper?

-sub surface application of dispersants

2. Is this information available? If not, what R&D needs will fill the gaps?

Decision maker info need	Info available? (Y or N)	In white paper? (Y or N)	**R&D Need**
Bioaccumulation of dispersants	Some (levels unspecified)	N	Yes
Toxicity of dispersants	Acute toxicity data;		Acute toxicity data along with chronic toxicity
Composition and formulation of dispersants CBI similar to pesticides	N	N	NCP need-product schedule requirement/regulatory revision
Communication addressing concerns about human and environmental health and safety from dispersants without publically disclosing composition and formulation			-Develop strategies for establishing trust with risk management agencies -Develop appropriate risk comparisons and analogies for oil spills and dispersants and then strategies for communicating those (environmental and human health)
Adequate resources to sustain communications about dispersants			
Technical specialists need a more direct link to agency officials and review before release			
EPA explicit approval of specific dispersants through sub part J (toxicity and effectiveness) regulation			
Dispersant effects on wildlife aside from death			

Communication needs assessment: top three needs at time of spill and in what format for political (elected and appointed) officials at the federal, state, and local levels			Political/appointed stakeholder Survey: what are political leaders (local, state, federal) regarding their expectations/ wants/needs/desires at the time of a spill with regard to dispersant use and the format that they want to receive it in (verbal brief, report, video, etc) and distribution (e.g., youtube, facebook) and strategies for implementation Public stakeholder survey: what are political leaders (local, state, federal) regarding their expectations/ wants/needs/desires at the time of a spill with regard to dispersant use and the format that they want to receive it in (verbal brief, report, video, etc) and distribution (e.g., youtube, facebook) and strategies for implementation
Communicate why it would or Wouldn't be used			
Making sure everyone is onboard or why they aren't			
Communicate a lucid, succinct description of NEBA			Environmental literacy through communicating the risk to stakeholders. What does the public expect and want to know and how do they want to receive it? (regional concerns) Develop messages that convey the continuum of response from preparedness through restoration
Communication of the process of trade-offs and the benefits of the decisions made for the long-term gain			
What can and cannot be done in spill response-expectation management in technical response			Research project to better define realistic roles and response opportunities for volunteers (affiliated and non affiliated) How to engage local government? Study opportunities for connections between NCP and FEMA- channel for engagement

			Evaluate ICS for inclusion/consideration of local government
Specific communication strategies for communicating the rightness of the decision to the public, media, congressman, and other officials			
Setting reasonable, realistic expectations for/from public and officials			Study to assess local community commitment to participate in oil spill preparedness and response (local community organizations, organizational networks, and individuals)
What the public expects from a spill of this magnitude (communicating that the environment won't return to "pristine" conditions			
People safety, stop the source, and mitigate/reduce environmental impacts			Developing a message to display RPs goals before, during, and after spill events
Impact to historical and cultural resources (which are non-renewable; e.g., wooden ship wrecks, tribal concerns)			Risk communication with cultural sensitivity and understanding
Risk communication for renewable resource communities has direct impacts on their economic wellbeing (perception vs realities) on a regional basis			
Development – fund workshops that involve academics as to the structure of oil spill response at natural hazard center annual workshop			For academic risk communications/disaster research

Breakout Session 2 notes:
-Litigation reduces transparency
-

-Decision makers have to agree to use dispersants, preauthorization (EPA- right to veto; Resource trustees-right to veto; NOAA, dept of commerce, DOI, potentially affected states/tribes). RP initiates idea, FOSC starts decision approval process
    -Need unanimous approval
-What information is needed to send up the food chain
-Need for response community to address change in focus/views around oil spills
-Politics slowed down response, but may not have changed actual response measures conducted
-Internal information verse public perception and vocalization (social media and word of mouth)
        -miscommunication or misunderstanding of information
- How do you maintain proprietary information from disclosure yet use the information for decision making

-no reason to have a dispersant on the list if it's ineffective
-no decision is a decision – no dispersant use. Couln't make up their minds fast enough
-Empower the people (prince William sound regional council)
-Reporter perspective: what the public wants to know: Who's in charge, what's in it, what effects does it have? Perception of industry and regulators in cohort
    -Exercise is crafting a public relations strategy
    -Public can't make informed decisions- difficult to communicate when agencies are "keeping industries secrets." Issue is that it's not disclosed that it's by law and not voluntarily "keeping secrets."
    -Explain polluter pays concept
    -Be transparent about decisions and why. Explain trade-offs
    -Identify interested individuals (e.g., reporters) and cultivate them.
    -Be aggressive about follow-up.
    -Point reporters towards geoplatform
    -redundancy with knowledge out there (e.g., alerting everyone to the amount of sampling conducted)
-

Breakout Session 3: Prioritize R&D Needs

Fill out template for each R&D need discussed in previous two breakout sessions. (i.e., Session 1 & 2 – included in white paper and to fulfill decision makers needs)

1. Conduct a needs assessment study (survey) for external stakeholders

    a. <u>Political/appointed stakeholder Survey</u>: what are political leaders (local, state, federal) regarding their expectations/ wants/needs/desires at the time of a spill with regard to dispersant use and the format that they want to receive it in (verbal brief, report, video, etc) and distribution (e.g., youtube, facebook) and strategies for implementation
    b. <u>Public stakeholder survey</u>: what are political leaders (local, state, federal) regarding their expectations/ wants/needs/desires at the time of a spill with regard to dispersant use and the format that they want to receive it in (verbal brief, report, video, etc) and distribution (e.g., youtube, facebook) and strategies for implementation
    c. Identify steps to address stakeholder needs and expectations, examples:
        i. (e.g., Develop strategies for establishing trust with risk management agencies)
        ii. Sources of information
        iii. Would like more information from preferred sources
        iv. Address delta between UC and external stakeholders
        v. Study opportunities for connections between NCP and FEMA-channel for engagement
        vi. Evaluate ICS for inclusion/consideration of local government
2. Conduct mental model research to elucidate environmental literacy with regard to dispersants and oil spills, environmental trade-offs, human health and seafood safety issues
    a. Environmental literacy through communicating the risk to stakeholders. What does the public expect and want to know and how do they want to receive it? (regional concerns)
    b. Develop appropriate risk comparisons and analogies for oil spills and dispersants and then strategies for communicating those (environmental and human health)
        i. For example relevance of lab studies to field conditions during an incident
    c. Develop messages that convey the continuum of response from preparedness through restoration
    d. Identify the degree of commitment from local communities in getting involved and being part of the response to develop bridges of trust for oil spills and the use of dispersants
3. Regional perceptions of spill response, dispersants and seafood safety.

1. Prioritize the R&D needs. (from highest #1 to lowest priority)

Template:

Research Topic 1	Conduct a needs assessment study (survey) of external stakeholders for spill response literacy, dispersant information needs and expectations and recommendations for future preparedness and response
Objectives	Supply laypeople (political/elected officials/general public/local stakeholders) with credible information they need to make informed judgments about risk to health, safety, and environmental tradeoffs associated with oil spill response including dispersant application
Guidelines (including whether lab/field study, etc)	Identify what the information needs are based on stakeholder group perspective [culturally sensitive] and develop recommendations for mechanisms to meet this information need and expectations using multiple research methods (e.g., focus groups, surveys, structured interviews, etc)
Issues/Problems	Acknowledge external (general public) stakeholder perception that unified command inherently involves a conflict of interest (for example transparency on the release of proprietary ingredients) [N.B. more to be added]
Application to decision making process	yes
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	2 year
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	high

Research Topic 2	Research methods to effectively communicate, educate stakeholder groups (general public) with regard to dispersants and oil spills, environmental trade-offs, human health and seafood safety issues
Objectives	Identify specific content and delivery channels and mechanisms for providing additional information for internal and external stakeholders. Translate scientific issues relating to oil spills, spill technologies, and dispersants into something tangible for the general public by narrowing the gap.
Guidelines (including whether lab/field study, etc)	Field applications including nominal group processes, two-way exchange Intent is for research topic 1 to inform research topic 2
Issues/Problems	-Overcome barriers of stove piping specialized knowledge. -This topic cuts across multiple issue topics.

	-Solutions and products will need to be maintained/updated/revisited periodically -Need to reevaluate periodically (e.g., every 5 years) -Cultural/geographic sensitivities
Application to decision making process	This fosters interagency and scientific collaboration
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	2 years or more
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	High

<u>Research Topic 3</u>	Regional perceptions of spill response, dispersants and seafood safety
Objectives	To determine attitudes and behaviors relative to consumption in restaurants and household purchases.
Guidelines (including whether lab/field study, etc)	Field study
Issues/Problems	Address the continuing consumer fear of GOM seafood
Application to decision making process	Provide information to target communication of seafood testing and monitoring to reluctant consumers and inform local seafood associations
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	1 year
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	Medium

Notes:
Public perception Wants versus needs (research need 1 vs 2)
SETAC- exposure studies and relevancy to actual concentrations seen in the environment

- Review sources and roles relating to safety and health of the environment
- Study dispersed oil versus the dispersants alone- this message has to be adequately communicated
- Data being published that isn’t relevant to the actual application of dispersants

- Characterize for the general public a lab study versus what’s actually seen in the field
- Developing a message to display RPs goals before, during, and after spill events
- Risk communication with cultural sensitivity and understanding
- For academic risk communications/disaster research
-

Dispersants and Human Health

Breakout Session 1: Review White Papers

(1) Discuss significant omissions (data, references, topics, and current knowledge). Discuss whether irrelevant information is included?

Omissions:	Type: (data, reference, topic, current knowledge)
-Pathways of exposure for each compound -Dermal, inhalation, oral	
-Detection limits	
-Interactions of compounds and exposure to some individual compounds from other sources	-NIOSH has 5 rodent studies published in Journal of Toxicology -Corexit 9500a inhalation, dermal and CNS studies
-Background for discrete locations	
-Mechanisms, additive effects and biological significance	
-Exposure groups -risk communication	
-Biological markers (metabolites)	
-Composition and fractionation of dispersants	

Irrelevant information: (list below)

- (N.B., Introduction-harmonize introduction across white papers)
    - Introduction-numbers of dispersants and oil and amount dispersed etc. harmonize that information
- Distillate fractions of petroleum (pg. 3; half way down second paragraph)
    - Initial focus was constituents in crude oil. Reviewer asked for this information
    - Dispersant and crude oil mixture.
- Table 2 pg 22- typo on exposure.
- Correction/clarification on propylene glycol?
- Consistency amongst routes of exposure- effects may be mechanistically similar, yet it may be difficult to extrapolate routes of exposure from an effect

Review the R&D needs presented in the white paper. (list below)

- Interaction of oil and dispersants

- Combination of oil, dispersants and the environment and their influence on uptake
- Long term studies of workers exposed to crude oil
- Studies on total mixture exposure and toxicology and **how** does it relate to workers/workforce. Need to show effects on HUMAN health.
- In-vivo and in-vitro studies
- Differentiate between irritant and something with permanent effects.
- Exposure assessments, how do you measure these
    - Biological markers
- Composition and fractionation of dispersants
- Safety and efficacy of dispersants
- Health literacy

Additional Notes (9/20/11)
-Focus on compounds of concern in corexit. Literature review
-Little information on concentrations that may be seen by the public. Took the approach from mammalian view.
-Don't know anything about dose, sensitive populations, or interactions with compounds
-How to monitor exposure-one of biggest challenges
-Exposure information
    -what information is needed to get exposure limits
-Actual exposure from exposure data, what is the relevance from a toxicology profile (bioavailability, etc)
-Public perception and health effects related to dispersants
-Propylene glycol ?

-occupational exposure limits –conceptually think about data this way or detection
-Levels of detection

-<u>NIHS Gulf study</u>: 25-50,000 people to participate (volunteers, NOAA, CG, etc)
    -questionnaire low to high exposures ; routes of exposure (dermal, inhalation)
    -epidemiology is separate
    -exposure levels to agents of interest
    -Model exposure (e.g., proximity to aerially applied dispersants, clean up efforts near shore-tar balls)
        -TPH and individual chemicals

-Exposed group – baseline information (control group) who may work near/around oil products (e.g., diesel) regularly.
-How do low levels of dispersants influence how chemicals will act in the environment

-Some individual compounds in dispersants can be found in everyday household compounds (e.g., toothpaste, hand sanitizer, suntan lotion)
    -Don't often look at interaction of compounds not individual compounds.

-How to study interactions of compounds and oil in a retrospective study on humans may prove very difficult.

  -methods to predict or consider potential interactions

-Golf course sand, paints, have agents (e.g., DOSS) that are point sources of a compound, but they are found in higher concentrations after rain events.

-Where dispersant meets the oil is where the interaction takes place and where should be studied.

-Ingestion verse dermal exposure for some compounds can influence exposure limits.

-Descriptive hazard identification

-systematic methodology- perception showing a compound is commercially available

-Important from a human perspective with exposure groups: comparisons with others. Biological significance

-NIOSH- 55 gallons of corexit: 5 published papers in journal of toxicology

  -many workers showed signs of breathing difficulties (symptoms that are also from heat exhaustion).

  -respiratory, dermal, and oral exposure to corexit and/or oil

  -Rodent exposure- respiratory exposure, corexit applied as aerosol, does constrict the airway and increases responsiveness to drugs targeting cardiac function. Also alters change in synaptic patterns (no true long term CNS studies)

-Range of potential receptors for effects and factors for reducing the effects

-Biomarkers, baseline, biomonitoring for workers (workers showing VOCs in blood yet misinterpreting the source of those VOCs- e.g., smokers)

  -NIOSH paper on biomonitoring (Protecting Workers in Large-Scale Emergency Responses: NIOSH Experience in the deepwater horizon response. Kitt, Decker, Delaney, Funk, Halpin, Tepper, Spahr, Howard. JOEM Vol 53, nUmb. 7. July 2011.

    -Urine is a source for biomarkers, many compounds can be excreted in urine

-Must be HAZWOPER trained to deal with haz waste-need physical in advance. Could use these for baseline studies. A physician could be trained/alerted on what to look for in that pre-screening physical

-No case of hemolysis in RBCs in humans even after overdose (link between mouse exposure and human exposure). No hemolysis, no cancer in rats.

-Full disclosure of composition of Dispersants for public perception and toxicology

  -Have specific releases, privacy remains intact but toxicological results are released

-Safety and efficacy standpoint on dispersants

Breakout Session 2: Decision Makers Perspective

(use table below to record discussion of both questions)

1. What information do decision makers need to know to address the possible uses of dispersants in future spills? Was this addressed in the white paper?

- Informing workers of risks. Training for safety, proper PPE. Access to care. Ensure community understands opportunity for exposure. Performing evaluation of public coming in contact with materials. Making recommendations to public. Getting information to public regarding safety of air, water, sediment. How will dispersants affect vulnerable population (e.g. infants, elderly, others with health issues)?
- Consumers of seafood, seafood safety.
- Health hazard evaluations.
- Comprehensive assessment of a safety program. Focused on workforce.
- Information coming from a credible, trusted source to the public.
- Sharing data, helping to make informed decisions.
- Environmental conditions. Knowing mechanisms and exposure routes. Exposure assessment. What to monitor for, how to monitor with what equipment. Testing and monitoring protocol to evaluate public health.
- Concern of **not** using dispersants. Not using dispersants can lead to more health concerns than not.
- Mental health effects. Reassuring people that they are safe, and not at a risk.
- Public health literacy. Understanding who will be affected and how.
- CME, how to diagnose health issues. Exposure assessment. What to monitor for, how to monitor with what equipment. How will dispersant affect those with prior health issues?
- Public understanding of what risk means. How much risk will the public accept? How can they themselves control that risk?
- Hazard information for what is known. Concentrations of oil.
- Managing uncertainty with public.
- How toxic is oil, is that a result of dispersant? Hazard for mixture.
- Organizing health affect/physical & chemical information of chemicals in oil and dispersants. Conveying that information to different levels of educated public. Compiling information to make it available.
- Understanding public needs and concerns. What questions are being asked?
- Protocol. What to know about hazard communication, what do you need to do for exposure assessment, and what to do to control exposure levels. Having protocol to be prepared for future spills.
- Group of toxicologist give a report to make use of dispersant. Whether or not dispersant is safe.
- EPA can create list of appropriate dispersants for different spill conditions. No need for proprietary information.
- Finding area between not giving out any information, and being viewed as untrustworthy. And giving out all the information and having issues with public health literacy.

- Create incentive for producer of dispersant to give health and safety information. Create a commercial advantage to be safer.

2. Is this information available? If not, what R&D needs will fill the gaps?

Decision maker info need	Info available? (Y or N)	In white paper? (Y or N)	R&D Need
Factual information and synthesis			Compilation of factual information • Dispersant or its constituents • Effects of chemical and mixtures if possible • Seafood safety • Sensitive population • Laboratory information, testing • Literature (routes of exposure, baseline, etc.) • Identifying uncertainties • Worker safety • Mental health/psychosocial stress • Dispersant lists • Application parameters/limitations of dispersants • Expert panel • Known repositories • Current requirements for protecting and proprietary information • Regulatory framework ; interim guidelines if lack of policy • Chemical and physical properties of the dispersant or its components

Hazard identification and exposure scenarios			• Environmental characteristics • Volatility • Droplet size • Half-life • Physics of application and aftereffects • Ranges of doses. • Dose determination and bioavailability • Routes of exposure (e.g. dermal, respiratory, ingestion) • Vulnerable people and species • Encounter probability(likelihood of exposure)
Worker/public safety			• Medical clearance and preplacement evaluation • Enhanced injury data collection and reporting system. I.E. study design. • How to interpret information from exposure assessment (qualitative and quantitative) • Bio-monitoring decision matrix • PPE selection, use and compliance. • What happens if things go wrong • Just in time safety training • Mixed chemical exposure • Exposure control (e.g. administrative and engineering controls) • Instrumentation • Protocol and process • Access to primary care and environmental health expertise
Communication and literacy			• Public • Credibility, transparency and trust • Response community • Doctors • Audience vs. issue Ethnic or subsistence

			populations • Putting information in context of other risks • Uncertainty of what we know, and what we do not • Sharing of information, proactive and reactive • Identification of the professional experience required to address dispersants (e.g. hygienists, physicians, toxicologists, etc.) • Dealing with misinformation/ misconceptions • Anticipated questions • Basic understanding of Risk
Additional science on dispersants			• Toxic effects of dispersant formulations • Oil dispersants mixtures • Synergistic effects? • Identification of ranges for a chemical in a formulation (adjustments for safety in uncertainty)
Trade offs			• Consequences of using or not using dispersants • Human health vs. environmental health vs. commerce • What we know, what we don't know (uncertainty) • Approach (precautionary principle, risk-benefit, risk-risk) • How to use what information we have, knowing the considerations
			•

- Establish toxicity individual dispersant formulations for human models, mammalian models.
- What is likely maximum exposure?

Toxicological

- How do the biological affects in mammalian systems of dispersant oil/mixtures compare to those predicted or measured by exposure to individual components alone.
    - Dispersants vs. ingredients
    - Oil vs. dispersed oil
    - Acute, repeat, longer term exposures
    - Target pulmonary, cardiovascular, CNS, and immune response
        - Synergistic and additive effects
- Better characterization of toxicological profiles of additional dispersant products in mammalian models
- Develop an understanding the biological affects (health hazards) of the dispersants as a formulation and a target agents (oil)
- Determine the short and long term human health impacts from various routes of exposure and various ranges of exposure for each dispersant that is available for use.
- Determine the short and long term human health impacts of dispersed oil.
- Can we measure or develop standardized animal invitro or insilico models that can be used to evaluate the toxic effects for human health.

Epidemiology

- To study the health effects in known exposed human populations.
- To develop relevant biological markers of exposure and guidelines for responsible use of the biomarker.

Exposure

- Can we measure or develop models to estimate exposure to dispersants and or dispersed oil to human populations
    - Occupational
    - Resident
- Develop an upper bound of exposure of the variable exposure scenarios associated with the dispersant use
    - Environmental
    - Occupational

Breakout Session 3: Prioritize R&D Needs

1. Fill out template for each R&D need discussed in previous two breakout sessions. (i.e., Session 1 & 2 – included in white paper and to fulfill decision makers needs)

2. Prioritize the R&D needs. (from highest #1 to lowest priority)

Template:

Research Topic	Epidemiology
Objectives	• To study the health effects in known potentially exposed human populations (dispersant manufacturing and response and remediation application). • To develop relevant biological markers of exposure and guidelines for responsible use of the biomarker.
Guidelines (including whether lab/field study, etc)	Lab and a field based exercise
Issues/Problems	Dealing with humans Identification of large enough exposed population Appropriate controls, validation of relevant biomarker
Application to decision making process	Human health risk assessment, potential bio-monitoring,
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	>2 years
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	High, could be millions

Research Topic	Exposure
Objectives	• Can we measure or develop models to estimate exposure to dispersants and or dispersed oil to human populations

	- Occupational - Resident - Develop an upper bound of exposure of the variable exposure scenarios associated with the dispersant use - Environmental - Occupational
Guidelines (including whether lab/field study, etc)	Lab and field
Issues/Problems	Access or gather existing information
Application to decision making process	Exposure control, potentially operational decision making, risk communication
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	1-2 years
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	Medium

Research Topic	Toxicological
Objectives	- Determine the biological affects in mammalian systems of dispersant oil/mixtures and compare to those predicted or measured by exposure to individual components alone. - Dispersants vs. ingredients - Oil vs. dispersed oil

	o Acute, repeat, longer term exposures o Target pulmonary, cardiovascular, CNS, and immune response ▪ Synergistic and additive effects • Better characterization of toxicological profiles of additional dispersant products in mammalian models • Develop an understanding the biological affects (health hazards) of the dispersants as a formulation and a target agents (oil) • Determine the short and long term human health impacts from various routes of exposure and various ranges of exposure for each dispersant that is available for use. • Can we measure or develop standardized animal in vitro or in silico models that can be used to evaluate the toxic effects for human health.
Guidelines (including whether lab/field study, etc)	Laboratory, models
Issues/Problems	Proprietary information Selection of the appropriate model and endpoint Formulations of oil, dispersants and/or mixtures
Application to decision making process	Accurate for hazard identification Proof of principle Importance of mixtures Maintain an appropriate schedule of dispersants Criteria for selection for a safe and effective dispersant Better incorporation of safety data
Length of Time of Project (<1 yr; 1-2 yr; >2 yr)	Various, depends on scope
Total Cost Estimate($) [High= >$400,000; Med =$100,000 – $400,000; Low = <$100,000]	High

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SCIENCE GAPS

RISK ASSESMENT, COMMUNICATION AND MITIGATION