Workshop Report for "GoMRI Contributions to Dispersant Science"
Core Area 2: Fate of Oil and Weathering
November 16-20, 2020

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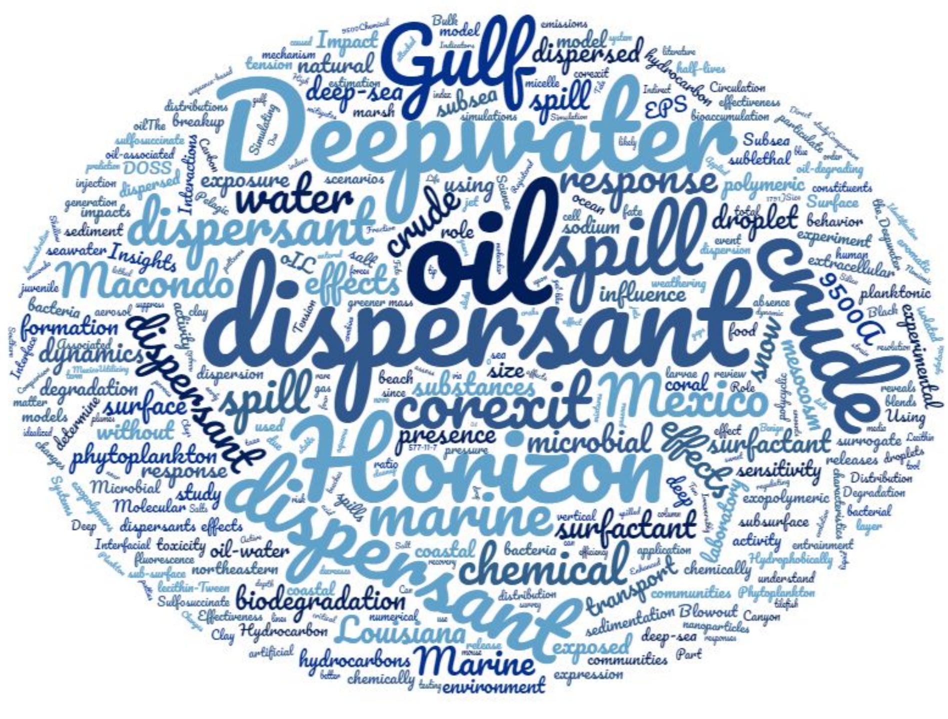

*Prepared using keywords from GoMRI dispersant papers

EXECUTIVE SUMMARY

The Deepwater Horizon (DwH) oil spill was the largest accidental marine oil spill in US waters in the petroleum industry history at the time in which it occurred. On April 20, 2010, an explosion on the Deepwater Horizon oil rig—located in the Gulf of Mexico, approximately 41 miles (66 km) off the coast of Louisiana—and its subsequent sinking on April 22 resulted in the death of 11 individuals and a total discharge over 87 days of more than 133 million gallons of crude oil. A massive response ensued to protect beaches, wetlands and estuaries from the spreading oil utilizing skimmer ships, floating booms, controlled burns and 1.84 million US gallons (7,000 m^3) of oil dispersant. Pre-dating any litigation or subsequent penalty money, BP almost immediately committed $500 million over a 10-year period to create a broad, independent research program conducted at research institutions primarily in the US Gulf Coast States. This program was the Gulf of Mexico Research Initiative (GoMRI), and it provided $50 million/year to research projects that investigated the impacts of the oil, dispersed oil, and dispersant on the ecosystems of the Gulf of Mexico. GoMRI funded multiple research consortia and small investigator grants from 2010 to 2020 with the ultimate goal to improve society's ability to understand, respond to, and mitigate the impacts of petroleum pollution and related stressors of the marine and coastal ecosystems, with an emphasis on conditions found in the Gulf of Mexico. Part of this understanding includes investigating the role that dispersant and oil mixtures played in ecosystem impact.

As part of the series of synthesis efforts directed at the impacts of the Deepwater Horizon oil spill, GoMRI hosted a virtual synthesis workshop entitled "GoMRI Contributions to Dispersant Science" the week of November 16th, 2020. GoMRI has made considerable investments in different research areas related to dispersants and its associated impacts. The intent of this workshop was to summarize and synthesize this research conducted by GoMRI scientists and to identify where the body of knowledge can inform future research on dispersant technology, response scenarios and human and environmental impacts. The workshop was not intended to fully summarize and synthesize the body of knowledge of dispersant science over the last decade, rather review the "state of the science" through the lens of GoMRI contributions over the last ten years. The National Academies of Sciences, Engineering and Medicine released a report in early 2020 "The Use of Dispersants in Marine Oil Spill Response" that reviewed over 1,000 studies on various aspects of dispersant use, interactions and impacts. The goals of this workshop were to position the collective GoMRI research within the context of the current state of the science of dispersants, while supplementing the NASEM report with relevant and actionable results from GoMRI-funded research. Presentations and discussions during the workshop also identified some emerging questions spurred by this research.

Given approximately 18% of GoMRI's research portfolio was directly related to the fate and effects of dispersant and this report attempts to transfer these findings into relevant and actionable applications in future spill scenarios. The workshop was attended by a wide cross

section of organizations and people with valuable data and expertise to contribute. The full agenda and attendee list are provided in this workshop report as appendices. The workshop was divided into 14 sessions, addressing a wide range of topics from operational considerations to providing the perspectives on human physical and mental health implications. The final section of the report provides the reader with recommendations for future research that include experimental standardization, best practices and more rapid sampling frameworks for human health impacts.

DISCLAIMER: While we included the discussions that took place after the presentations to capture the scientific process, some points have not been peer-reviewed and should be interpreted as educated opinion unless otherwise supported by a reference.

LIST OF ACRONYMS

ADDOMeX	Aggregation and Degradation of Dispersants and Oil by Microbial Exopolymers
API	American Petroleum Institute
ARRT	Alaska Regional Response Team
ART	alternative response technologies
BOP	blowout preventer
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
CAFE	Chemical aquatic fate and effects
CERA	Consensus Ecological Risk Assessment
CEWAF	chemical enhanced water accommodated fraction of oil
CFR	Code of Federal Regulations
C-IMAGE	Center for the Integrated Modeling and Analysis of Gulf Ecosystems
CMEDS	Consortium for the Molecular Engineering of Dispersant Systems
CPUE	catch per unit effort
CRA	Comparative Risk Assessment
CROSERF method	Chemical Response to Oil Spills: Ecological Research Forum
CRRC	Coastal Response Research Center
CWA	Clean Water Act
DCEWAF	Diluted chemically enhanced water accommodated fraction of oil
DDO	dispersants and dispersed oil
DIVER	Data integration, visualization, exploration and reporting
DOC	Department of Commerce
DOI	Department of the Interior
DOR	dispersant to oil ratios
DOSS	dioctyl sodium sulfosuccinate
DSD	droplet size distribution
DwH	Deepwater Horizon
DWG	dispersants working group
EPA	Environmental Protection Agency
EPS	exopolymer substances
FOSC	federal on scene coordinator
GCMS	gas chromatography-mass spectrometry
GDS	Global Dispersant Stockpile
GNOME	General NOAA Operational Modeling Environment
GoMRI	Gulf of Mexico Research Initiative
GOR	gas to oil ratio
GRIIDC	Gulf of Mexico Research Initiative Information & Data Cooperative
HEWAF	high energy water accommodated fraction of oil
IOGP	International Association of Oil & Gas Producers
IOSC	international oil spill conference
IPIECA	International Petroleum Industry Environmental Conservation Association
LC50	lethal concentration where 50% are killed
LEWAF	low energy water accommodated fraction of oil

LL50	lethal loading killing 50% of exposed organisms (for non-soluble compounds)
MOA	Modes of toxic action
MOSSFA	Marine Oil Snow Sedimentation and Flocculent Accumulation
NASEM	National Academies of Sciences, Engineering and Medicine
NCP	National Oil and Hazardous Substances Pollution Contingency Plan
NEBA	Net Environmental Benefit Analysis
NIOSH	National Institute of Occupational Safety and Health
NOAA	National Oceanic and Atmospheric Administration
NRC	National Response Center
NRS	National Response System
NRDA	Natural Resource Damage Assessment
OPA90	Oil Pollution Act of 1990
OSHA	Occupational Safety and Health Administration
PAH	polyaromatic hydrocarbons
PPE	Personal Protection Equipment
RP	responsible party
RRT	regional response team
SEAMAP	Southeast Area Monitoring and Assessment Program
SIMA	Spill Impact Mitigation Assessment
SMART	Special Monitoring of Applied Response Technologies
SONS	spill of national significance
SPME	Solid phase micro extraction
SSC	Scientific Support Coordinator
SSDI	sub-sea dispersant injection
TAMOC	Texas A&M oil spill calculator
TDR	turbulence dissipation rate
TLM	target lipid model
TPH	total petroleum hydrocarbons
TU	toxic units
TUHH	Technical University of Hamburg at Harburg
USCG	United States Coast Guard
UV	ultraviolet
VOC	volatile organic compound
WAF	water accommodated fraction of oil
WOD	oil in water dispersion
WSF	water-soluble fraction of oil
WSH	water-soluble hydrocarbons
WSIH	water-soluble individual hydrocarbons

SESSION SUMMARIES

The format of the agenda was designed to provide a buildable knowledge base of dispersant use, chemistry, policies, and impacts. Some of the content presented here is/was not solely GoMRI-funded, but it is presented and summarized here to provide background to assign context and applicability to the academic research.

SESSION 1: Introduction and Goals

Dr. Antonietta Quigg commenced the workshop with introductory remarks summarizing the workshop's intent to review the "state of the science" through the lens of GoMRI contributions over the last ten years. The catalog of GoMRI research related to dispersants is substantial; there are more than 200 GoMRI publications that use the word dispersant, ranging from field to experimental. As of 10/06/2020, they can be categorized into:

1. Type of study
   128 lab-based studies
   14 mesocosm based studies
   18 based on field measurements/observations
   18 modeling studies (various)

2. Study topic (chemistry, physics, exposure (biological)
   54 physics (mostly new dispersants and modeling)
   53 ecology/exposure employing WAF and/or CEWAF
   35 chemistry some WAF and CEWAF some new dispersants
   16 MOSSFA (many WAF and CEWAF)
   review papers (various)

3. Experimental focus
   61 organism focused (26 bacteria, 19 plankton (various), 10 invertebrate, 6 vertebrae
   4 human health
   35 new dispersant formulations
   30 droplet and dispersion focus
   10 chemical degradation, photodegradation

"Rules of Engagement" were shared to assign guiding principles during the workshop:

1) Assume best intentions, but do not assume anything else.
2) Ask questions to better understand anything that is unclear or troubling.
3) Listen when others speak.
4) Share your views and concerns in the room.
5) Treat each other with kindness and tolerance first.
6) Take care of yourself.

SESSION IIA: Role of Dispersants in Oil Spills - Operational Considerations

Session II was divided up into two sections. Session IIA was to review the factors considered when assessing if, when, and how dispersants are to be used operationally in response. Dr. Tim Nedwed from ExxonMobil and Dr. Victoria Broje from Shell were the presenters for Session IIA.

In responding to an oil spill, there are well-defined assessments that must be made early on in the response effort. Although each spill is unique and provides its own set of considerations, what is defined is the number of tools first responders have at their disposal: remote sensing and monitoring, mechanical containment and recovery, *in-situ* burning, dispersants, as well as various shoreline protection and cleanup techniques. For large offshore spills, dispersants are the most effective response tool due to the time scale of the response. Mechanical recovery and containment and *in situ* burning must be initiated manually and require substantial transit time to the spill site. Dispersants can be applied to a spill area from a vessel or an airplane, thus, the response time is ultimately only limited by the speed of the airplane. Of course, the prepositioning of an adequate dispersant supply through the Global Dispersant Stockpile (GDS) is an important factor in determining the response time. Because there is a narrow time window for dispersant use due to the oil weathering process, transit time to the site is a critical factor.

In the case of an offshore spill, there are limitations for mechanical recovery based on the scale of the spill and sea-state conditions. Difficulty is encountered for boom utility and *in situ* burning at a sea state of three to five feet. Also, since mechanical recovery vessels can only advance at a speed of about 3/4 of a knot when collecting the oil, they have limited oil encounter rates compared to aerial dispersants that can treat a large area of a slick quickly. Industry's "rule of thumb" is that booms/skimmers are responsible for about 10-30% of oil recovery. However, in reality this number is closer to 2-15% for large offshore spills (Etkin and Nedwed 2021). Since a majority of oil spills are relatively small and are located close to equipment depots, mechanical recovery remains the primary and most commonly used response tool.

Surface dispersant application is a viable response option due to the speed at which they can be applied, the ability for dispersants to remove oil from the water's surface and the promotion of biodegradation. In the case of sub-sea dispersant injection (SSDI) during DwH, this was the only tool available to treat the oil at the source. SSDI is *now* part of the routinely planned and exercise training activities for offshore wells. In the case of a subsea blowout, the possible aims of subsea dispersants injection are to: 1) potentially treat 100% of the oil at the source, 2) protect response workers by limiting surface volatile organic compound (VOC) concentrations, 3) allow 24/7 operations even in high seas because application at the source is not impacted by sea state, 4) prevent surfacing of oil and 5) remove oil from the environment through biodegradation.

For future studies, the challenge of translating lab-based oil spill fate and effects into real world implications must be integrated in the experimental design. Differences can lead to (1) dispersed oil appearing more toxic than it is, (2) unrepresentative dispersed oil biodegradation tests, and (3) negative bias inherent in closed-system dispersant-effectiveness testing. Equilibrium is a significant issue with chemical enhanced water accommodated fraction of oil (CEWAF) and high energy water accommodated fraction of oil (HEWAF) toxicity testing because the droplets in these systems provide a reservoir for dissolved components as dilutions are made. That is, even though the dissolved components are diluted in the dilution series used for toxicity testing, droplet oil is carried into the dilutions and provides a reservoir for more dissolved components so they are not all completely diluted (Forth et al. 2017) at least until the droplet reservoirs are exhausted. This makes HEWAF and CEWAF oil appear more toxic than it would be in the real world where there is no equilibria. Further, the droplets provide a reservoir for losses during the actual tests. That is, if a dissolved phase molecule adsorbs on a lipid, evaporates, or biodegrades, it is rapidly replaced by the same molecule leaching out of the droplet oil to reestablish equilibrium.

There was discussion around this point, particularly in terms of the dilution factor, and the opinion that laboratory-based oil exposure studies do not allow for representation of field dilution conditions. As such they are often conducted with oil and dispersants concentrations 100s times higher and for much longer durations than would typically exist in the field. For the subsurface plume, however, this formation exhibited behavior akin to a chemostat in its integrity and prevented dilution in the similar scope to the surface environment. Additionally, laboratory-based studies that allow for equilibrium can be useful for estimating the "worst-case" conditions or for representing short term or local conditions. A caution should be exercised when extrapolating conclusions of the laboratory results to the real-world conditions without additional interpretation, e.g. modeling discussed later in this summary.

In determining the "best" response option, the primary objectives are to: 1) protect the health and safety of the public and responders, 2) minimize overall environmental impact, 3) minimize economic impacts, and 4) communicate with and engage stakeholders. A NEBA (Net Environmental Benefit Analysis) concept of "do no harm or minimize harm" should be applied to the selection of optimal response options that would be most effective if protecting resources and expediting ecosystem recovery. In this assessment, both environmental and socioeconomic risks are considered. There are three main approaches to assess risk:

1. In the Consensus Ecological Risk Assessment (CERA) framework, a response scenario is developed with specific detailed information on oil composition, toxicity, and the possible weathering processes the material will experience. The scenario, response options and evaluation of the impact of the response options are developed by a diverse group of stakeholders whose primary goal is to look at the impacts of no response versus response options. The impacted environment is divided up into a number of compartments (e.g., water, shoreline, socio-economic resources, etc.) (Fig. 1). Each compartment must be defined by its representative population or resources and its relationship to the other defined compartments. Connectivity between compartments during the SIMA (Spill Impact Mitigation Assessment) and CERA is flexible, and both the nearshore and offshore compartments can be incorporated with the relevant organisms of interest. This results in a risk-ranking matrix where the amount of resource that is affected is quantified by a percent of a population/habitat affected and the rate of recovery. A developmental history of CERA and subsequent methods such as SIMA can be found in the resources listed in Table 1.

Environmental compartment		Representative population/resources
	Seabed benthic zone	Burrowing organisms
Water column	Near seabed demersal zone	Flatfish
	Deep water pelagic (>400 m)	Round body fish
	Mid-water pelagic (<400 m)	Round body fish
	Upper water layer (<20 m)	Plankton
	Nearshore water (<10 m)	Coral reef
	Sea surface	Seabirds/sea mammals
Shoreline	Nearshore sediments	Seagrass
	Wetlands	Burrowing organisms
	Rocky shores	
	Sandy shores	
socio-economic resources	Coastal tourism	
	Inshore fisheries and aquaculture**	
	Mid-water fisheries**	
	Deep water fisheries**	
	Seawater intakes	
	Maritime recreation	

Figure 1. IPIECA/IOGP CERA framework.

2. The SIMA (Spill Impact Mitigation Assessment) approach is relatively new in the way it collects the knowledge of experts and stakeholders and converts their expertise and recommendations into numerical values. Similar to CERA, SIMA identifies compartments within the impacted environment and assesses different impacts with and without response measures. When the impacts are assessed, the process uses consensus of experts to assign impact numbers relative to each other. As the group discusses response options and looks at each compartment, the questions that are addressed are 1) will this response technique hurt or help, and 2) how well is it expected to mitigate the impact from a spill, or what additional impacts can it cause. These assessments are based on expert knowledge and best available information and translated to a numerical matrix by assigning an impact coefficient and multiplying this by a mitigation factor. Scores for each response technique are then summed up across all compartments. The higher positive SIMA score indicates likely ability of a response technique to mitigate impact from the spill. Negative SIMA scores indicate that a response technique may result in a greater damage than an unmitigated slick.

3. The Comparative Risk Assessment (CRA) is a new computationally intensive framework and it has only been used twice. This assessment is similar in process to CERA in terms of identifying compartments and identifying the representative populations within that compartment. However, the CRA takes a more quantitative approach that involves complex 3D numerical modeling and calculating the volume of water and area of the water's surface that was impacted by the oil spill. They are then overlapped by the density of resource categories in the area. A risk coefficient is used based on population's sensitivity, vulnerability and recovery rates. As in most risk assessments, the animals that are slowest to reproduce and those that are long-lived appear to be at greatest risk and come up at the top of protection priority (French-McCay et al. 2018, Bock et al. 2018, Walker et al. 2018).

Table 1. Reports and sources related to CERA, SIMA and CRA history and development. See references for full citation.

Document Title	**Organization/Year**
Guidelines for Ecological Risk Assessment	EPA, 1998
A Framework for Net Environmental Benefit Analysis for Remediation or Restoration of Petroleum-Contaminated Sites	Efroymson et al., 2003
Developing Consensus Ecological Risk Assessments: Environmental Protection in Oil Spill Response Planning	Aurand et al., 2000
Choosing Spill Response Options to Minimize Damage: NEBA	IPIECA Report Series, Volume 10, 2000
Standard Guide for Determining Net Environmental Benefit of Dispersant Use	ASTM Standard F2532-13
Response Strategy Development Using Net Environmental Benefit Analysis	IPIECA-IOPG, 2015, *revised* 2016
Guidelines on Implementing Spill Impact Mitigation Assessment	IPIECA-API-IOGP, 2017

The NEBA process with the above pathways is quite distinct from the NRDA (Natural Resource Damage Assessment) process. The NEBA framework attempts to integrate all available knowledge on the impacts of oil in different compartments, and evaluates the ability of response techniques to mitigate them. It starts with an assumption that oil is already in the environment and seeks to find an optimal response solution, recognizing that none of the response techniques are 100% effective and all of them come with their own risks. This analysis can be performed reasonably quickly using high level information at a population and ecosystem level and does not require extensive scientific analysis or information about individual organisms. This method can be used for populations of organisms with a wide range of life-histories.

SESSION IIB: Role of Dispersants in Oil Spills – Coordination of Response

Session IIB discussed the various aspects of coordinating the response from the participating federal agencies. Mike Sams is the Incident Management and Preparedness Advisor for the Eighth Coast Guard District, and he provided an overview of the statutory and regulatory authorities related to dispersant use. Dr. Paige Doelling is the NOAA Scientific Support Coordinator (SSC) for the Houston, Galveston, and Corpus Christi.

During the DwH response, the key entities involved were the members of the region 6 regional response team (RRT). The team includes 15 members of Federal agencies and state representatives and is co-chaired by the United States Coast Guard (USCG) and the Environmental Protection Agency (EPA). There is no one entity that is solely responsible for oil spill preparedness and response; this is a team effort. This team is called the National Response System (NRS) and includes the National Response Center, the National Response Team, 13 Regional Response Teams, Federal On-Scene Coordinators, Area Committees, State and Local Governments, Joint Response Teams with neighboring countries, Regulated Industry and Special Teams. The legal framework for the response is governed by the Clean Water Act (CWA) as amended by the Oil Pollution Act of 1990 (OPA90). The response actions developed through the legal framework are implemented through the National Oil and Hazardous Substances Pollution Contingency Plan (NCP). The EPA is responsible for updating the NCP, and this includes Subpart J that discusses response technologies, including dispersants. EPA is also tasked with establishing and maintaining the NCP product schedule.

In the Gulf of Mexico, dispersant use is pre-authorized for surface application, but not for nearshore or subsea injection. For surface and aerial applications, the offshore boundary for application is from the 10-meter isobath or 3 nautical miles, whichever is farthest from shore to 200 nautical miles. The Federal On Scene Coordinators' (FOSC) pre-authorization includes the plan to engage the RRT personnel in order to ensure that the team is making the best decision per incident (refer to the RRT-6 Pre-Approval Guidelines and Checklist). Nearshore is defined to be closer than 3 miles to shore, and authorization to use dispersants this close to shore must include concurrence of the RRT (refer to RRT-6 Near Shore Environmental Dispersant Expedited Approval Process and Checklists). Before the DwH oil spill, the response teams did not have a framework for subsea dispersant use, and this process was developed in real time during the response. In fact, the only time the FOSC is authorized to use subsea dispersants without RRT concurrence per 40 CFR 300.910(d) is when it "is necessary to prevent or substantially reduce a hazard to human life." In any other instance for the use of dispersants subsea, the FOSC cannot authorize use without the consultation & concurrence of the RRT. In determining if surface application of dispersants is appropriate, the SMART (Special Monitoring of Applied Response Technologies) protocols are applied. Briefly,

Tier I:
A trained observer, flying over the oil slick and using photographic job aids or advanced remote sensing instruments, assesses dispersant efficacy and reports back to the Unified Command.

Tier II:
Tier II provides real-time data from the treated slick. A sampling team on a boat uses a monitoring instrument to continuously monitor for dispersed oil 1 meter under the dispersant-treated slick. The team records and conveys the data to the Scientific Support Team, which forwards it, with recommendations, to the Unified Command. Water samples are also taken for later analysis at a laboratory.

Tier III:
By expanding the monitoring efforts in several ways, Tier III provides information on where the dispersed oil goes and what happens to it.

- Water depth ≥ 10 meters and no less than 3 nautical miles from nearest shoreline.
- The SMART controller/observer should be over the spray site before the start of the operation.
- If possible, a DOI/DOC-approved marine mammal/turtle and pelagic/migratory birds survey specialist will accompany the SMART observer, but the operation will not be delayed for that individual
- If dispersant platform is an aircraft, spray aircraft will maintain a minimum 1000-foot horizontal separation from rafting flocks of birds. Caution will be taken to avoid spraying over marine mammals and marine turtles.
- The FOSC is to notify the RRT as soon as practicable after the approval is given to the RP.

After DwH, eight response exercises for different well locations in the Gulf of Mexico were conducted. In seven of those hypothetical scenarios, the use of SSDI was approved to mitigate loss of source control. Note that this is not the only tool that is used during the response exercises. All of the tools in the toolbox are used to reduce potential impacts and expedite ecosystem recovery. The activation summaries can be accessed here: https://www.epaosc.org/site/site_profile.aspx?site_id=5083.

The primary role of the NOAA SSC is to act as the chief technical advisor for the United States Coast Guard. This is a purely advisory role not responsible for decision making. The SSCs have a team of specialists, the Scientific Support Team, and they are specific to how the response is carried out. The team seeks consensus on scientific issues to ensure the response is both **efficient and effective**, provides official oil spill trajectories, assists with risk assessment, and assesses tradeoffs, as demonstrated by the NEBA process referenced in Session IIA.

The first and most important tasks that must be addressed right after a spill is to frame and scale the problem as is defined in Figure 2. How big is it? What are our options? Is it so far offshore that mechanical recovery isn't an option? What is the risk category? The response process moves through the five "W"s:

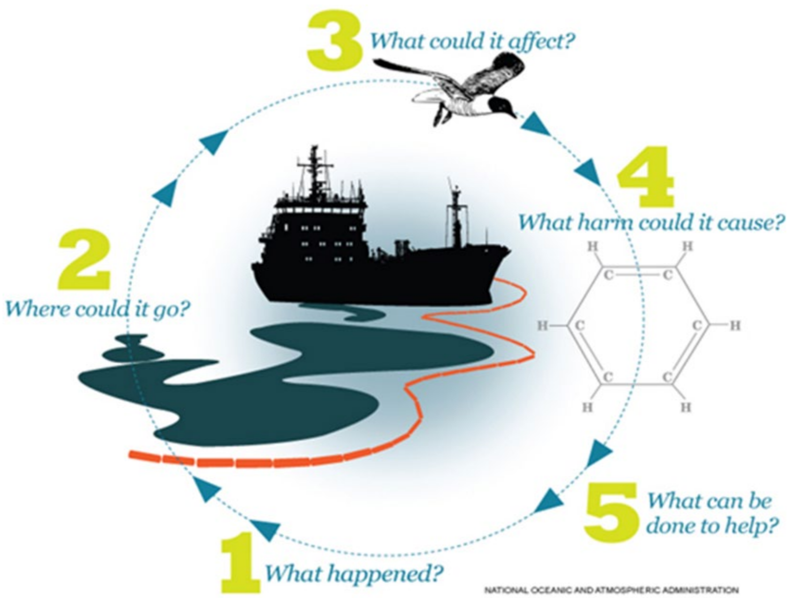

Figure 2. Guiding questions for oil spill recommendations (NOAA's Office of Response and Restoration).

1. What happened?
2. Where could the oil go, and when could it get there? (for this we use GNOME – General NOAA Operational Modeling Environment)
3. What could it affect?
4. What harm could it cause? Different components cause different toxicological effects.
5. What can be done to help? When the spill is offshore, mechanical recovery is the first choice and dispersant application is secondary. Note that due to sea state, mechanical recovery can be difficult.

Dr. Doelling used the spill at Green Canyon 248 in May of 2016 to demonstrate the decision-making process used to determine if surface dispersant application was to be used. Dispersants are classified as alternative response technologies (ART). The decision-makers are aware that when the decision is made to use dispersants, the consequence is that priority protection is given to the organisms at the shoreline at the expense of the organisms in the water column and benthos. In the case of the Green Canyon 248, dispersants were considered but ultimately not approved; this decision was made by Coast Guard. Trajectory studies showed that shoreline landing of oil was not projected beyond tarballs, and excellent conditions existed for on-water recovery. Additional questions to be addressed in advance of dispersant use are: (1) Is the oil dispersible? (2) Is shoreline impact projected? (3) Are organisms at the sea surface at risk, and if so what is the risk? 4) Are skimming assets and associated vessels available? 5) Is the weather conducive to application?

Q. *Is there a limit for sea state (wave/wind) for deciding when dispersant application is no longer necessary?* **A.** Some oils will naturally disperse, noting that oils are very different. A strong storm will disperse oil, but responders cannot rely on mother nature to disperse oil for us.

Q. *Can you collect oil at well head*? **A.** The DwH blowout is a life-threatening event to a corporation, and since then, significant investments have been made to prevent a blowout. In the event that a blowout does occur, the response team will do everything to collect the flow. However, collecting oil at depth far from shore oil is not that simple.

Q. *How many significant oil spills have occurred since 2010 in Region 4 and 6*? **A.** There was a discharge during hurricane Nate in MS Canyon 209. In region 4 there have been no significant oil discharges since 2010. Dispersants have not been used in the Gulf of Mexico since 2010.

Q. *Were subsea plumes observed in the Green Canyon spill*? **A.** No. There was no dissolved gas and it was a small leak from a pipeline rather than a wellhead.

Q. *What is the relationship between NEBA/SIMA and the framework by which NRDA is assessed*? **A.** NEBA/SIMA are used during planning and the species of concern are identified by the expert stakeholders. The impact to these species after an actual event is what would be assessed during the NRDA. In the NEBA/SIMA the goal is to minimize the impacts on critical elements of the ecosystem by selecting an optimal response option.

Q. *How do we monitor in the field the effectiveness of dispersant*? *What are the current measurement tools and capabilities?* **A.** With SSDI there is a specific monitoring protocol. Specific parameters are measured both in the subsurface and on the surface to determine the effectiveness. For DwH, survey protocol was developed both near and far from well-head to see where the subsurface plume was in an effort to track it. This monitoring was not simple with varying vertical profiles of currents. Fluorometry was used to monitor oil movement during the Green Canyon and MC 209 spills. For SSDI one of the key parameters indicative of how efficacious dispersant is droplet size. The current guiding protocol that outlines the efficacy of surface dispersant use is called SMART (Special Monitoring of Alternative Response Technologies). Bejarano et al. (2013) evaluated the SMART protocol implemented from the M/V International Peace by analyzing water samples for TPHs, TPAHs and Corexit and found that the field assessments on dispersant effectiveness and the results from the analyses were in reasonable agreement. However, in an upcoming paper at IOSC, Nedwed et al. (2021) summarizes the current issues and flaws associated with it. In the current monitoring protocols, efficacy is measured by fluorometers from vessels. After surface dispersant application these fluorometers measure oil concentrations and track where the dispersed oil is moving. However, identifying the oil presence and motion is quite difficult due to the ability of the dispersed oil to rapidly dilute, the orthogonal relationship between surface slicks and subsea oil transport, and the extent of weathering that occurs between release and measurement. Recommendations on the horizon for monitoring are to revise the SMART protocols, enlist and advance remote sending technologies, use *in situ* mass spectrometry with cameras, LISSTs and other sensors in a swarm formation. These sensors would also provide measurements on determining marine snow conditions or identify a marine oil snow sedimentation and flocculent accumulation (MOSSFA) event. This might be a charge for the academic community.

SESSION III: Oil Dispersion at the Oil/Water Interface

Session III was developed to give participants context related to the complex interactions between oil, water and dispersant at the oil/water interface. This is a key topic that is relevant to many other sessions in this workshop. The presentation was shared between Ron Larson (University of Michigan), Alon McCormick (University of Minnesota) and Vijay John (Tulane University). The talk was divided into two sections; the first focused on the description of fundamental physicochemical processes at the oil-water interface upon addition of dispersants and the second section was directed toward technologies developed by researchers funded through GoMRI. A key aspect of the presentation was the conceptual aspects of molecular and nanoscale observations that could be related to the macroscopic behavior of dispersant systems.

To provide a preface to the observations, the presentation started with the fundamental perspective of the Gibbs Phase Rule which indicates that in a two-phase liquid-liquid system of oil and water, the solubility of the oil in the bulk aqueous phase is fixed if the temperature and pressure are defined. This is true, regardless of whether the oil is in the form of a surface layer or as droplets stabilized by surfactants. The question then arises as to the actual amount of surfactant partitioning to the oil-water interface. Given a typical dispersant to oil ratio of 1:20, a rough calculation shows that less than 1% of the surfactant added is needed to saturate the interface of 50 μm droplets. The excess surfactant partitions into the bulk phases. In the case of Corexit, the water soluble nonionic polyoxyethylene (20) sorbitan monooleate surfactant (Tween 80) partitions to the water phase and could exist as oil-swollen micelles. The excess oil soluble nonionic surfactant sorbitan monooleate (SPAN 80) will partition into the oil, while the twin tailed anionic surfactant, dioctyl sodium sulfosuccinate (DOSS) which is fully soluble in oil while sparingly soluble in water is expected to partition into the oil phase and form water-in-oil microemulsions. As these surfactant containing droplets travel through the water column, conventional interpretations indicate that as dilution occurs, the surfactant partitions out from the interface and into the bulk water phase, eventually leading to a surfactant free interface. But as Dr. Larson pointed out, experiments at Carnegie Mellon showed that there is a degree of irreversibility in Tween adsorption at the oil-water interface and that dilution does not remove the surfactant from the interface (Figure 3). Molecular simulations showed that this is a consequence of the

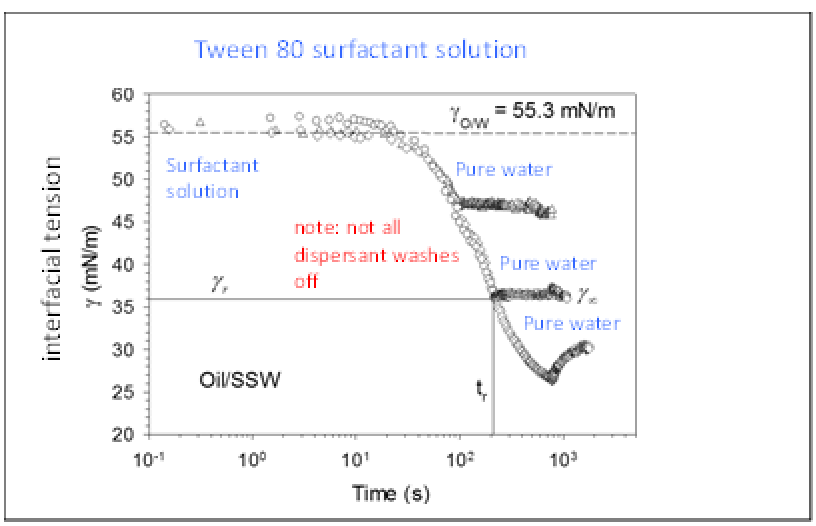

Figure 3. Partial reversibility of surfactant adsorption (Reichert and Walker, 2013).

large head groups of Tween forming networks at the interface that inhibit desorption.

The implications of surfactant retention at the oil-water interface are noteworthy. It is typically understood that dispersion increases the interfacial area for bacterial consumption of oil, implying that rates of biodegradation would be enhanced in systems with dispersed oil rather than a surface layer of oil. But if dispersants create a "new" interface, one that is decorated with surfactants, the direct correlation of surface area and biodegradation rates may not hold. High resolution electron microscopy reveals prolific bacterial attachment to a pristine oil-water interface and the generation of biofilm. However, work at the University of Rhode Island showed that a Corexit laden interface exhibits a significant inhibition of such bacterial attachment (Abbasi et al. 2018a, b) although biodegradation is not impeded (Omarova et al. 2018; Figure 4). This brings up the possibility that biodegradation may have alternate pathways using oil solubilized in biosurfactant micelles or in the bulk water phase.

Figure 4 Bacterial growth at a pristine flat oil-water interface. On the right is a high resolution cryo scanning electron micrograph of cells and biofilm. From Omarova et al. (2018)

The second section of the presentation focused on the concepts of new and alternative dispersants to Corexit. Phospholipids are double tailed natural lipids and have many of the interfacial properties of DOSS. In the search for environmentally benign alternative to DOSS, it was shown by researchers at the University of Maryland that soybean lecithin, a natural and inexpensive phospholipid could be combined with Tween 80 to formulate dispersants with dispersion efficiencies equivalent to Corexit (Athas et a. 2014). Additionally, droplets containing the lecithin-tween surfactant were more stable against coalescence compared to Corexit. Dr. McCormick presented studies that showed the role of spontaneous emulsification using the lecithin-tween system again pointing to the potential use of these systems (Riehm et al. 2017). Gel-like dispersants are useful to improve adherence to weathered oil and minimize solvent use. Such a gel formulation containing DOSS, lecithin and Tween was described that stayed buoyant for extended periods thus increasing oil encounter rates (Owoseni et al. 2018).

Finally, there is the concept of particle stabilized emulsions where natural clays could be used to form Pickering emulsions and stabilize droplets against coalescence (Omarova et al. 2018). Such systems could be particularly effective in subsurface applications because the turbulence supplies sufficient energy for emulsion formation. The drawback of particle stabilized emulsions is perhaps the fact that the droplets are relatively large and will not be colloidally stable in the water column. The presentation showed new aspects of coupling surfactants and particles (Owoseni et al. 2015). The use of tubular nanoclays (halloysites) containing surfactants in the lumen of the tube is a distinct possibility. Such systems could deliver the surfactant in aqueous slurries and the formulation avoids the use of organic solvents. Particles at interfaces also help to anchor bacteria and promote the formation of extensive biofilm.

Salient points of the discussion follow.
There was discussion about the translation of observations in the laboratory to the infinite dilution of the ocean. One thought was that equilibrium considerations do not really apply as surfactant is stripped off the droplet through rapid dilution. On the other hand, plume transport of the droplets may imply that dilution in a plume environment may not be instantaneous. Equilibrium considerations in these environments are useful to understand the fate of the dispersants and to understand local conditions around droplets. The observation of DOSS with stranded oil on ocean sediments is indication of surfactant being carried with the oil. The stripping of surfactant from oil droplets remains an unanswered question.

The question of the adoption of new dispersants was discussed in detail. It was noted that the large stockpiles of existing dispersants (Corexit, Dasic and Finasol) implied that newer surfactant formulations would not be easily adopted as there were additional questions of deployability and liability. It was noted that there might be a possibility to combine newer concepts of dispersants (e.g. particles at interfaces) with existing dispersants to introduce more easily accepted modifications. This would be particularly true if there is a synergism between newer concepts and existing dispersants.

SESSION IV: Exposure Methodologies: WAF and CEWAF

Dr. Terry Wade from Texas A&M University discussed various techniques and methodologies in carrying out exposure studies for aquatic organisms, summarizing what has been used with the associated drawbacks and how the scientific community can advance the process of developing and standardizing exposure methodologies.

It is near impossible to mimic real-world conditions in the laboratory. The ocean is heterogeneous due to the presence of natural materials in the water column. Organic carbon exists in a continuum from truly dissolved through colloidal size to larger particles. For standardizing sampling, two phases are considered in most studies: particulate (>0.5 microns) and dissolved (<0.45 microns). The dissolved phase can include bacteria and viruses, and the particulate phase includes phytoplankton and zooplankton. While using synthetic seawater may provide for a simpler medium, interactions between these particles will be missed. The following discussion highlights some of the methods that have been used to form solutions for micro and mesocosm studies.

1) WSH (Water Soluble Individual Hydrocarbons) or WSF (Water Soluble Fraction) of oils – glass beads, mineral particles or sediment are placed in a glass column. As seawater descends through the media, non-soluble oil adsorbs to the glass beads or mineral particles and the resultant water only contains the dissolved fraction of hydrocarbons.
2) WOD (Oil in Water Dispersion) – oil is added to water, mixed (stirred or shaken) and this solution is then used for dosing studies.
3) WSIH (Water Soluble Individual Hydrocarbons) or WSF - silicon rings are soaked in individual hydrocarbons or mixtures of hydrocarbons to produce WSIH or WSF. The rings can then be rinsed with methanol and put in test systems.
4) WSF – oil is injected into a silicon tube and placed in seawater, creating a WSF.

Many common protocols for developing a WAF or CEWAF solution generally follow the CROSERF (Chemical Response to Oil Spills: Ecological Research Forum) method but with modifications ranging from small to substantial (Aurand and Coelho 2005). In terms of the types of oils used for the toxicity studies, multiple test oils were sampled from various sources. NRDA collected source oil from the riser as well as from two slicks (non-weathered and weathered). This oil was processed to remove water and mixed to produce homogeneous aliquots. It was also artificially weathered until it lost approximately one third (33 to 38%) of its mass. This process is referred to as "topping" the oil and this material was used for the toxicity studies (Forth et al. 2017). Making WAF, CEWAF and HEWAF (high energy WAF) requires the introduction of energy into the system. Note that as in the real world, heterogeneity is an issue even in experimental setups as demonstrated by the large standard deviations of PAH concentrations in the mixtures.

Mesocosm experiments are necessary since it is not permitted to intentionally spill oil into the environment in the United States. A mesocosm is a controlled experimental system to examine natural environments, and these can be validated by comparing results to findings from field studies. The GoMRI-funded consortia ADDOMEX used mesocosms to produce marine oil snows. Researchers produced the EPS (exopolymer substances) as this is a natural phenomenon, including in the WAF, CEWAF and controls (Quigg et al. 2016). To produce the WAF, a 25 ml mixture of Macondo surrogate oil and Corexit 9500 with a ratio of 20:1 was added to a 130 liter baffled recirculation tank. Stirrers were initially used for energy input, however, this resulted in a breakdown of the EPS into smaller particles. Nutrients and microbes were added to some of the mesocosms to observe interactions. For dosing experiments, WSF was produced by placing oil filled tubes in stirred mesocosms with seawater for 24 hours. The tubes were then removed from the system and compared with mesocosms where particulate oil was present. No slicks were observed in the dissolved treatment (details are in Bera et al. 2020).

Parting messages: (1) Oil and water do not mix but we try, (2) Chemical analyses are necessary to assess exposure, (3) Variability is expected: chemistry less than biology, (4) Mesocosms replicates document variability, (5) Source, slick, artificially weathered and reference oil collection were valuable resources, (6) Purposely spilling oil in US is not allowed, and (7) Oil is a "natural" component of the environment.

The next presentation in the session was given by Dr. Susan Kane Driscoll from Exponent and was titled "Uncertainty in Assessing the Potential Toxicity of Oil is Influenced by Variability in Test Conditions". Although aquatic organisms can be exposed to oil via multiple routes of exposure, including absorption from water, direct contact (e.g., smothering), inhalation and ingestion, WAFs and CEWAFs are often used in laboratory toxicity tests to examine absorption from water. Uncertainty in assessing the toxicity of oil in laboratory tests is influenced by the concentration and composition of oil in WAF and CEWAFs, which varies among types of oil (e.g., fresh vs. weathered oil) and among WAF protocols (e.g., influence of mixing energy and addition of dispersants). For example, high-energy WAFs (HEWAFs) have been shown to have much higher concentrations of tricyclic PAHs, which are associated with early life stage toxicity in fish (Incardona et al. 2004), than other protocols (e.g. low-energy or moderate-energy WAFs). The presence of droplets also contributes to concentration variability. The magnitude of variability in concentrations is shown in Figure 5 where concentrations of $TPAH_{50}$ in MASS (unweathered MC252 oil collected from the Oil Barge Massachusetts on August 15, 2010) and CTC (slick oil collected from skimmers on July 19, 2010 stored on Barge CTC02404) are shown for low, medium and high energy scenarios, with and without Corexit, and with and without filtration (Kane Driscoll et al. 2016). These differences demonstrate the need for fully characterizing the concentrations and composition of PAHs and other constituents in WAFs, rather than reporting concentrations as % WAF or as concentrations of total PAHs. A statistical approach that was used to compare the similarity of laboratory WAFs to field samples collected during the active DwH spill period reported that the compositions of PAHs in most field samples (86%) were not similar to any of the laboratory WAFs (Kane Driscoll et al. 2016).

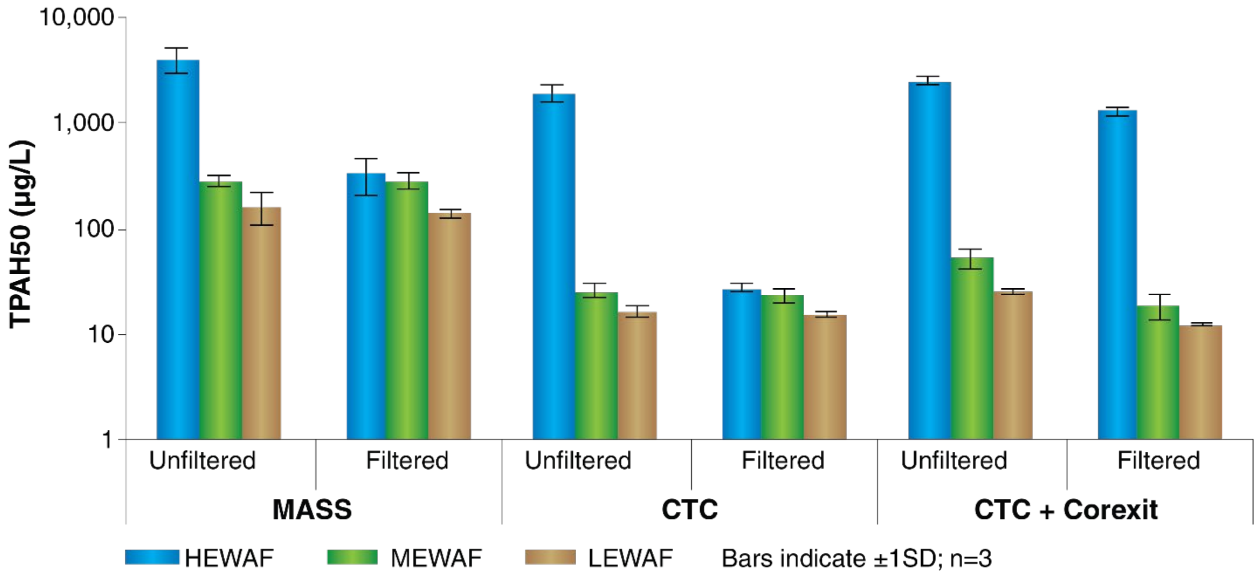

Figure 5. Variability in concentration of TPAH among WAF protocols (Kane Driscoll et al. 2016)

This result demonstrates the need for approaches that consider the variability in composition of laboratory WAFs in order to make predictions of toxicity under field conditions. Further analysis of available laboratory toxicity test data based on toxicity models that consider concentrations of individual constituents is recommended.

The next presentation was given by Joy McGrath currently with Environmental Resource Management titled "Oil Toxicity Modeling: Challenges and Modeling Framework". The aqueous exposure and toxicity of oil are evaluated using laboratory prepared WAFs and CEWAFs. With WAF and CEWAF preparations, several challenges must be overcome to successfully relate the observed effects on an organism to the chemicals the organism was exposed to and subsequently, relate these to environmental conditions. One challenge is that the exposure metric should be characteristic of the WAF composition and include detailed chemistry, rather than expressing on a percent WAF or TPAH basis. Toxicity expressions metrics on a percent WAF or TPAH makes it especially difficult when trying to compare studies from different researchers.

Another challenge is that the exposure metric should consider the differing toxicities of the individual chemicals in oil and in the WAF/CEWAF preparations. PAHs are considered to be the main causative agents of oil toxicity (Patel et al. 2020). The aqueous toxicities of individual PAHs vary by over four orders of magnitude and simply summing the concentration of individual PAHs on a mass basis is not appropriate and does not consider the differing toxicity of the individual components. Further, WAFs and CEWAFs include dissolved oil as well as neutrally buoyant oil droplets and chemical measurements are reflective of the total concentration of the dissolved and oil phase components. The dissolved oil is the bioavailable fraction that is readily available for uptake by the organism and responsible for organism effects. The presence of the oil droplets in the WAF and CEWAF preparations and measurements need to be considered when relating the measured chemistry to observed organism response. Research is still ongoing to determine whether or not these oil droplets are bioavailable.

Another challenge is that two different oil dosing methods are utilized; variable loading and variable dilution, which require different modeling approaches to interpret. In variable loading, oil and water are mixed (e.g., oil load A), equilibrated, and the bottom portion (which contains both dissolved and oil droplets) is used for the exposure laboratory experiments. This is repeated using different oil loadings (e.g. oil load B, oil load C, etc.). In the variable dilution treatment, oil and water are mixed, equilibrated, and the bottom portion is collected, typically representing 100% WAF. A portion of the 100% WAF is then diluted with water, re-equilibrated and the bottom portion is collected. If the ratio of 100% WAF and water is 50:50, then the resulting bottom portion is 50% WAF. This procedure is repeated using the diluted bottom portion until the desired dilutions for exposure are obtained. In variable dilutions, the oil droplets decline linearly with dilution. However, the dissolved concentrations do not decline linearly due to the re-equilibration process whereby the oil droplets behave as a source of oil that can dissolve.
The Petrotox is a framework that couples a fate and toxicity modeling approach for petroleum substances to overcome these challenges. It considers detailed oil chemistry, computes the dissolved oil concentration, and considers the differing toxicity of the individual components by expressing the toxicity on a toxic unit basis. This process would be applicable across different oil and oil weathering states.

SESSION V: Key Findings from the NASEM Report

Part of this workshop's charge was to provide the research community with updates to dispersant science since the release of the National Academies of Sciences, Engineering and Medicine's (NASEM) report on the Use of Dispersants in Marine Oil Response early in 2020 (NASEM 2020). While the GoMRI funded research was winding down in 2020, scientific findings related to dispersants are still currently being escorted through the peer review process. This session's goal was to provide the audience with the key concepts presented in the NASEM report from which to build on. The reader is referred to the additional dispersant reports from NASEM for further information. The leads for this session were Dr. Tom Coolbaugh with Applied Research Associates as the Program Facility Manager for the Ohmsett wave tank, formerly with ExxonMobil, and Dr. Steven Murawski with the University of South Florida. Both Drs Coolbaugh and Murawski served on the committee that generated the NASAEM report.

The NASEM study reviewed the most recent research on the efficacy and effects of using dispersants as a tool and evaluated the trade-offs associated with its use. The report also reviewed the human health component and found that the injury due to perceived impacts and fear is a real factor to consider. A key part of the NASEM study was to summarize information that can ultimately support the decision-making process that is used during the spill response. As a grounding statement, the ultimate goal is for the dispersant to promote small droplet formation and lengthen the amount of time these droplets are in the water column to promote dissolution and degradation. Much of the literature since the 2005 report focuses on the DwH spill, but the report is not a retrospective evaluation of that event. The modern formulation of dispersant has relatively low toxicity. Dispersant use is not supported in freshwater where there is no capability of further dilution.

The operation and response considerations were summarized in Session II of this workshop but it's appropriate to quickly review the general premise behind the motivation for dispersant application. Dispersants are applied to reduce the interfacial tension between oil and water that creates smaller droplets and increases the amount of time that an oil droplet stays in the water column. During this time, natural processes act on the droplet (biodegradation, weathering, etc.). During the DwH event, dispersant application was shown to decrease the concentration of volatile organic compounds at the sea surface thus increasing first responder safety (Gros et al. 2017).

RECOMMENDATION: A model hindcast of the VOCs generated around the Macondo Well should be performed to better validate models and understand processes affecting VOC concentrations.

Another major aspect of the NASEM report was to review existing data on toxicity studies. During this process, much of the effort centered around accessing, and contributing to, the

Chemical Aquatic Fate and Effects (CAFE) Database. The idea was to bring the historical data into the post-2010 context. A meta-analysis of current studies through 2017 brought the database and included GoMRI studies. Through the meta-analysis, the toxicity of various formulations of dispersants was collected and Corexit 9500 was found to hover around the average, with the full range from 1 to 10 ppm. The realistic issue is not the toxicity of the dispersant itself and its stand-alone effect, but the dispersant in combination with the oil. The report summarizes the wide range of test animals in the exposure studies. However, because of the types of dosing methods and metrics used to report toxicity responses, assessments of WAF vs CEWAF toxicities are a challenge. When test results from variable loading studies were used, the toxicity of CEWAF was comparable to that of WAF up to a lethal loading of approximately 100 mg oil/L. Above this oil loading, CEWAF appears to be more toxic than the WAF due to either higher concentrations of oil microdroplet in CEWAF relative to WAF, or the increased toxicity of CEWAF by the dispersant. This was a major finding and is detailed in Bejarano et al. (2014) and NASEM (2020; Figure 5).

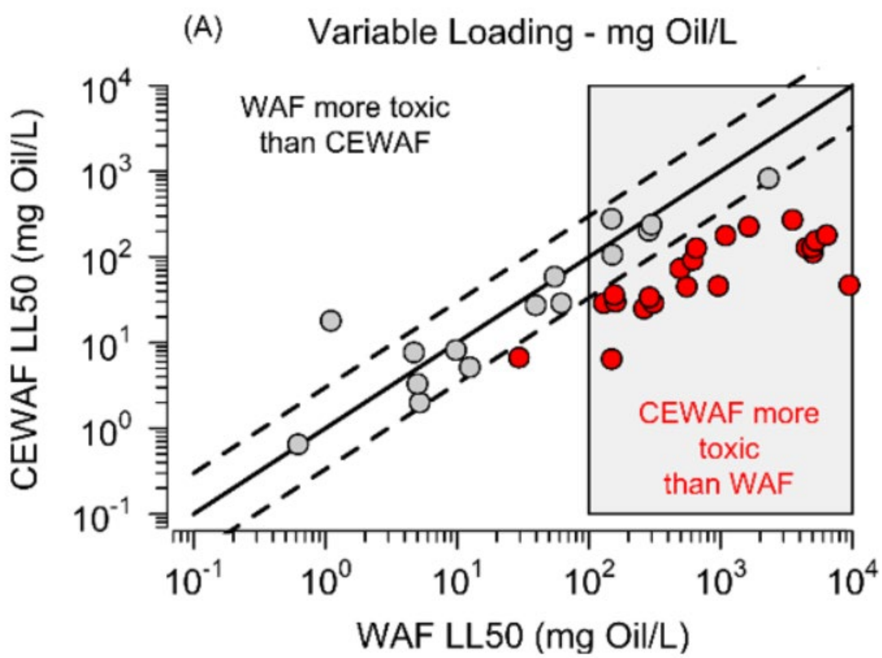

Figure 5. Data from Bejarano et al. (2014) and NASEM Committee's Appendix F.

In order to advance laboratory studies to extrapolate laboratory findings to field impacts, there are four key factors that need to be resolved: 1) concentration exceeding known acute or chronic toxicity thresholds for a specific oil; 2) duration of exposure above these toxic thresholds; 3) spatial and temporal distribution of marine life; and 4) species sensitivity to oil exposure above the acute or chronic toxicity thresholds.

RECOMMENDATION: The use of toxic units (TU) should be integrated into revised oil toxicity testing standards, evaluation criteria for models, and response option risk analysis. TUs make it possible to compare the toxicity of various mixtures of PAHs from different source oils and from mixtures that results from the differential solubility of oil constituents in seawater. The CROSERF methodology should be updated to reflect this.

Research has noted the role dispersants have in providing a mechanism for a significant amount of oil to settle to the seafloor. Sedimented oil through MOSSFA affects benthic organisms while surfacing oil can present hazards to surfacing animals through inhalation and aspiration. As discussed previously, VOCs may be reduced by dispersant application, however, this differential impact between oil and dispersed oil to wildlife and human health is not fully understood under field conditions.

The human health dimension related to dispersant use continues to be a concern, even in present day. There is concern amongst first responders related to their exposure to VOCs such as benzene, toluene, ethylbenzene, and xylene through direct inhalation or dermal contact. There has also been concern over how much exposure to dispersed oil is related to the consumption of seafood, and although there were concentrations of DOSS found in seafood, it was at very low levels. The more surprising impacts were the indirect psychosocial effects related to stress, primarily due to lack of transparency.

RECOMMENDATION: Biomarkers should be established for each dispersant formulation listed on the US EPA National Contingency Plan (NCP) Product Schedule. More robust reporting requirements should be improved for future spills to determine whether or not an exposure occurred.

RECOMMENDATION: The tools supporting the NEBA process that were discussed in SESSION II should be expanded to address health (e.g., response personnel, community) and socioeconomic (e.g., beach closures) considerations. These tools should be used to gain stakeholder input on local/regional priorities, expand awareness, and gain trust in the decision-making process.

In the existing framework, the research community has limited opportunities for real-world releases and associated response options. Studies have demonstrated that environmental conditions in the “real world” are different than the experimental designs in mesocosm studies. The community should be ready to take advantage of field studies through spills of opportunity. An example of this in the GoMRI community was the Hercules release. (GoMRI, 2013)

Q. *What were the best practices that came out of the human health issues related to perceived exposure? What will change with the next spill?* **A.** Industry learned a lot from last time; it is not the most trusted entity and partnerships need to be developed with more trusted organizations like academia. The psychological impacts where a novel part of the NASEM study. GoMRI has contributed to collecting this research through funding a synthesis workshop on human health and stress (Sandifer et al. 2020). Stress on the human population is cumulative and people in this region had experienced stress from other events (eg. Hurricane Katrina). The idea is to develop a human health observing system so a baseline dataset of human health can be referenced.

Comment: The NASEM report is not as specific in its recommendations for risk assessment. The report does not highlight whether or not more toxicity testing is important for future response decision-making and the community needs to get more data that can inform what response strategy to use. Studies on the toxicity of Corexit 9500 are plentiful. Instead, the focus should shift on getting more information to decision-makers in the form of a model for comparative risk assessment. These risk assessment models can return something quantitative on how a spill will impact an ecosystem. Toxicity test data needs to be scaled up to population or ecosystem effect.

INDIVIDUAL → POPULATION → ECOSYSTEM IMPACTS

There is no need to reinvent the wheel. This methodology already exists for pesticide use and from those studies, we've seen that there is a great amount of resiliency in the environment, especially if the environment is diverse (NASEM 2020).

SESSION VI: Impacts of Dispersants on Marine Organisms and Communities

The main charge of this session was to provide a summary on the different toxicity testing that has been done with dispersants through each of the different taxonomic groups and to examine what role these groups play in food webs. What are the practical applications for future spill response, and what are our knowledge gaps?

The first part of the presentation was given by Dr. Carys Mitchelmore at the University of Maryland Center for Environmental Science at the Chesapeake Biological Lab. In observing the full manner of oil exposure, defining exposure is the primary critical step in how toxicological threats are translated. The challenge throughout toxicology studies is to link laboratory studies to field studies (Fodrie et al. 2014; Figure 6).

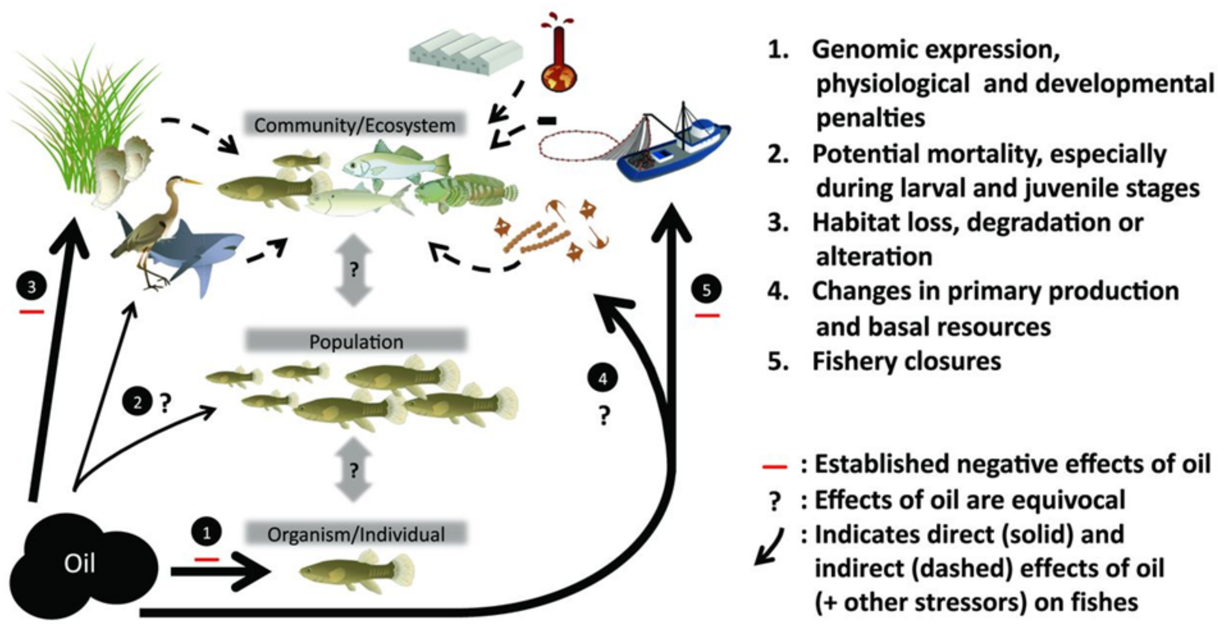

Figure 6 Large-scale effects from oil pollution occurs at multiple hierarchical levels (Fodrie et al. 2014).

A consistent paradigm regime often straddled in the workshop was identifying the question what the experiment is designed to answer and to distinguish between scientific research or research for spill response. This will steer the design and subsequent research questions. Existing research aims to answer how dispersant alters exposure routes and bioavailability of constituents in oil. As discussed previously, there are a number of methods for making up solutions with different energy regimes, oil to water ratios, DORs, filtered vs unfiltered using stacked system glass fiber filters, etc. The methodology determines how many and how much PAHs are available for exposure. For example, in the LEWAF, PAHs are in dissolved phase and in the HEWAF and CEWAF mixtures PAH concentration is driven by droplets. The implications of how these mixtures are developed depend on exposure routes of the organisms. The differentiation between dissolved and particulate oil is key for correct data interpretation (Forth et al. 2017). Another complicating factor is that as the exposure mixture settles, droplet sizes decrease over the duration of the exposure test. *Message: dispersants change the quantity, form and composition of oil chemical constituents.* It should also be noted here that in a closes system, oil droplets are allowed approach equilibrium with dissolved oil. This allows soluble components in the oil to approach solubility limits. In an open system, diffusion and advection deter the oil droplets and dissolved components from approaching equilibrium, implying that organisms in a closed system are exposed to much higher dissolved phase concentrations than they would in the real world (Forth et al. 2017, Wu et al. 2012).

Dr. Edward Buskey from the University of Texas Marine Sciences Institute discussed the potential trophic cascading impact that changes in phytoplankton population can have on the ecosystem in response to oil and dispersant exposures. These phytoplankton interactions are key to understanding the ecology of the open ocean. The impact of oil and dispersants on phytoplankton was very species-specific and there is evidence to suggest that the bacteria associated with this phytoplankton may reduce the toxic effects of oil and dispersants in some dinoflagellates (Severin et al. 2016; Park and Buskey 2020). In mesocosm studies using natural phytoplankton assemblages, researchers found that coastal phytoplankton species are more resilient than those in the open ocean (Doyle et al. 2020) and that phytoplankton response to oil and dispersant in the lab is dependent on nutrient availability, temperature and light availability.

In terms of trophic interactions laboratory studies found that marine protozoa are dominant grazers of phytoplankton and due to their rapid growth rate (1 division/day) they respond rapidly to phytoplankton changes. When investigating how exposure to various mixtures impacts growth rates, laboratory studies showed that exposure to oil, dispersed oil, and dispersant-only reduces the growth rate of protozoa, in descending order (Almeda et al. 2014a) and that ciliates are more sensitive to these mixtures than dinoflagellates. Microcosm studies using natural plankton assemblages from the Gulf of Mexico demonstrated that higher sensitivity to oil exposure by ciliate grazers on phytoplankton could lead to increases in population of potential red tide forming dinoflagellates (Almeda et al. 2018). Further microcosm experiments looking at the natural assemblages found that overall, exposure to WAF and CEWAF did not significantly change zooplankton abundance and biomass. The species composition changes, meaning there are ‘winners and losers’ but the overall biomass does not change due to increased diversity.

Laboratory studies have also determined that the larval stages of various zooplankton are more sensitive to toxicants and showed increased mortality to dispersed oil (ratio of 20:1) compared with single solutions of oil only and dispersant only (Almeda et al. 2014b). Exposure to oil, dispersant and mixtures had a negative impact on copepod egg production rate, fecal pellet production rates and egg hatching compared to controls. Zooplankton grazing also provides a mechanism for oil to reach the seafloor. They feed on small oil droplets and the oil is found in the fecal pellets which then sink (Almeda et al. 2016). This provides another exposure mechanism for deep corals which can impact their growth demonstrated by Mitchelmore et al. (*unpublished*). Due to their life histories, even short-term exposure to corals can produce long term impacts.

Dr. Martin Grosell with the University of Miami provided the next presentation with a review on how dispersants can impact fish health. Much of the research presented focused on the pelagic fish population of mahi-mahi as they are among the most sensitive when it comes to environmental perturbations, likely due to their high energy and aerobic demands. Not surprisingly, the larvae and embryonic stages are the most sensitive to perturbations. Laboratory studies were designed to investigate the extent to which Corexit 9500 alone is toxic to fish. Studies showed that only at DOSS concentrations significantly higher than those found in the environment were toxic (3-5 mg/L opposed to 2-12 µg/L). For the laboratory exposures to mixtures, the HEWAFs were prepared by "blending" oil and seawater, allowing mixture to settle for one hour, and using the aqueous phase as the medium. For the CEWAF mixtures, seawater and oil and dispersant were mixed at a DOR of 1:20, stirred for 18-24 hours, allowed to settle for 3-6 hours, and the resulting aqueous phase was used as the exposure medium. The LC50s for the early life stages of mahi-mahi showed no difference between the HEWAF and CEWAF exposures (Esbaugh et al. 2016). This demonstrates the difficulty in dissecting the impacts of oil and dispersant and dispersant alone. However, in looking at sublethal effects, laboratory studies showed that exposure to CEWAF mixtures resulted in decreased immune function, developmental deformities, reduced growth, and increased induction of a stress response gene (Greer et al. 2019, Mu et al. 2014, Jones et al. 2017, Ramachandran et al. 2004) by simultaneously monitoring the expression of tens of thousands of genes. In terms of mixing energies, for low energies, the addition of dispersants increases PAH concentrations by about 6.3-fold. Alternatively, for high energy regimes dispersant addition increases PAH concentrations by only about 1.6-fold; oil and dispersant mixtures have a greater effect on toxicity in lower energy regimes. This is significant because the 3-ringed PAHs, of which there are more of in the low energy conditions, are the compounds that are found to be most negatively impactful in association with sublethal effects on fish (Mager and Grosell, *unpublished*).

The next presentation was given by Dr. Adriana Bejarano from Shell that added contextual design to data integration and informing predictive modeling on how populations are affected. Laboratory experiments can offer a controlled environment from which to develop causal relationships, and those relationships can be used to inform model development for real world applications. To the end, public access to data and efforts to facilitate accessibility and proper use of the information will support model development. Examples of these databases are CAFE, NOAA's DIVER, and GoMRI's GRIIDC). This session presented a few case studies of how models can be developed to perhaps predict toxicity.
The Bejarano (2018) study data mined all of the toxicity studies (pre-2010 and until 2017) and summarized the species sensitivity distribution for Corexit 9500 exposure. In these studies, 64

species including standard and non-standard test species were exposed to Corexit 9500 and it was discovered that all of the newly tested species fell within the previous range of sensitivities. These results can be used to develop important communication and visualization tools. These tools that display the long-liner relationship between two species can be used for model development that can calculate the toxicity for other species that have not yet been test for a toxicity response. The models can help fill data gaps.

The current PETROTOX approach uses the Target Lipid Model (TLM) to model aquatic toxicity from petroleum products. In order to inform the model the user must know the chemistry of oil and the individual components in the oil to calculate the toxicity units (TU). The TU framework will allow standardization of the information that already exists in these databases and allow researchers to be able to compare results on a level playing field (DiToro et al. 2007). This framework also removes the influence of oil droplets which, as discussed previously, can complicate matter by falsely magnifying toxicity. The full intent of the TU framework is to be able to draw a 'lab to field' approximation (French-McCay 2002). The exposure quantification needs to be standardized by what is actually in the dissolved phase of the exposure media. In laboratory studies, the LL50 for certain species has a large range, but if the loading can be translated to concentrations by looking at what exactly is in the dissolved phase of the exposure media, by using SPME (solid-phase micro-extraction), mortality curves tighten and the relationship between mortality and concentration tighten (Letinski et al. 2014). This experiment was performed in Ohmsett where SPMEs were deployed at different depths and concentration of oil was measured with and without dispersants. A "threshold" concentration was defined and as time progressed, in the oiled case, concentrations were above this threshold just after the spill in only one instance, but witnessed increased exceedances for the case with dispersant, however, dissolved concentrations declined with time which is comparable to what one would expect to see under field conditions.

RECOMMENDATIONS:

- Standardized protocols/experimental design are key to promote comparison of datasets (i.e. mixing energy, dispersant:oil ratios); re-visit CROSERF, many updates/new methods etc.
- QAQC and minimum reporting criteria and data quality requirements would provide more toxicological data points suitable for inclusion in toxicity models;
- Extensive chemical characterization of the exposure test media is critical, minimum criteria of chemical analytes should be conducted at appropriate and multiple time points during the test.
- Investigations and chemical quantitation in dissolved and particulate phases (and maybe oil droplet quantity and size) should be performed.
- Toxicity and MOAs of unresolved fractions, other constituents, new oil types/dispersants?
- Include more than just LC50 and EC endpoints. Develop population models.

- Extract more from existing datasets. What is the question? Dichotomy of approaches: comparative toxicology vs. food web and environmental impacts → scientific investigations/MOAs vs. spill response needs.
- Laboratory studies are carefully controlled/characterized/standard test species. Studies to understand environmental impacts require site specific ecological relevant species and communities and conditions.
- Most studies conducted are with fresh oil / dispersant– more studies are needed on oil and dispersants in various ‘weathering’ stages and other transformation processes.
- Include environmental influences/natural variations/co-stressors as part of experimental design in toxicity tests – UV light, low oxygen levels, food or nutrient limitations.
- Timing of exposures - shorter durations, follow through recovery to identify latent and delayed effects. Experiments should employ environmentally-realistic and validated methods. Laboratory testing should consider environmentally relevant exposure scenarios based on post-spill field measurements.
- Toxicity data from time-variable exposures → provide endpoints for assessing effects at short exposure durations.
- Single hydrocarbon toxicity tests → Important for improving, calibrating effects models.
- Chronic toxicity data with deep sea species → longer exposures might be a concern under SSDI.
- Wave tanks/controlled trials → model calibration of effects on aquatic species under environmentally realistic exposures.

Q. *Was dispersant found on the seafloor or was it just oil? What was the distribution?* **A.** DOSS was found on corals. The DOSS is what drives the toxicity in C9500.
Comment: Perhaps the benthic impacts near the well were from the influence of failed top-kill? The top-kill certainly confused things in the nearfield. Note that the industry has put much effort in preventing spills since this kind of spill is company-ending.
Comment: The development of accurate algorithms for predictive models for toxicity is critical because it is quite difficult to capture variation of oil in the same field over time. Responders need to know what components in the solution are driving the toxicity.
Comment: It can’t be all about toxicity because some fish, even early in life stages, can metabolize PAHs. It is well known that PAH metabolism can create reactive oxygen species which can lead to, among others, lipid peroxidation and DNA oxidation, but metabolism also produces more water-soluble compounds that are easily excreted. A comprehensive model should look at the additive toxicity of these components. The TLM, as seen earlier, is able to predict toxicity based on concentrations of PAHs (McGrath and DiToro 2009, McGrath et al. 2018).

SESSION VII: Effectiveness of Surface Application and Deep-Sea Injection

Dr. Gina Coelho with Sponson Group, Inc. provided a presentation on the history of dispersant use and the efficacy of both surface and subsea dispersant application. For historical context, dispersants have been applied to more than 150 accidental oil releases with about 50 of those being major spills. Early dispersant formulations (i.e., in the 1960s) were highly toxic but are no longer used. Over the past several decades, modern formulations have been developed with low toxicity, and these are the products that are currently available for use. Some of the major events involving dispersant use include the IXTOC 1 spill in 1979 (a blowout in the southern Gulf of Mexico where aerial and vessel dispersant application was significant) and the Puerto Rican in 1984 (transport tanker leak of highly viscous oil) off the coast of California. The Sea Empress spill in 1996 was a heavily studied spill due its proximity to a shoreline. The Hebei Spirit of 2007 is notable because confusion and miscommunications in the initial response phase caused delays and the released oil became weathered to the point where dispersants were no longer a viable option. There is a limited window of opportunity for dispersant use. The 2009 Montara spill in Australia was a prolonged release over several months where dispersants were used routinely as a primary response option.

The decision to use dispersants must include these considerations:

(1) window of opportunity – highly weathered oil will not disperse as easily as freshly spilled oil

(2) dispersant-to-oil-ratio (DOR) – in order to establish a target DOR, responders need to know how much oil is in the response area. In DwH, the subsea dispersant injection (SSDI) DOR was theoretically calculated based on estimated flow rate, and was likely under-dosed since accurate flow rate information was not available during the early phase of the response operations

(3) application methods – responders must consider most appropriate means of application (vessel, aircraft, subsea), depending on the overall spatial scale of the spill, and based on other response strategies that are being implemented.

Real-time oil spill conditions will impact the effectiveness of a given dispersant operation. For example, the ability to mobilize dispersant assets to a remote spill location and the current weather conditions for a safe flight are just a few factors that must be considered. Other environmental conditions such as salinity should be assessed since very low salinities (e.g., below 15ppt) are not ideal for dispersant applications. Recent studies, both during DwH and in wave tanks, indicate that wave height should not be used as criterion because in some cases boat props can add the necessary energy for dispersal. In the Arctic, cold temperatures can increase window of opportunity because it slows down weathering.

Determining surface dispersant effectiveness during a response is difficult, and visual monitoring continues to be one of the important elements of monitoring. Visual monitoring falls within the first tier of SMART monitoring. The second tier of SMART monitoring, which involves small vessels measuring hydrocarbon concentrations, proved to be difficult during DwH because the vessels needed to "stand off" during aerial dispersant application, then traveled back to the spill location to take measurements. Typically, this time delay was 30+ minutes, during which time dilution or other natural processes may have occurred. As a result, the ability to adequately characterize the effectiveness of the operation was compromised because of safety considerations.

There have been many field trials designed to study dispersants over the past several decades. Those field trials, in combination with data from wave tank experiments have helped to inform modeling efforts to better understand the fate and transport of untreated and dispersed oil.

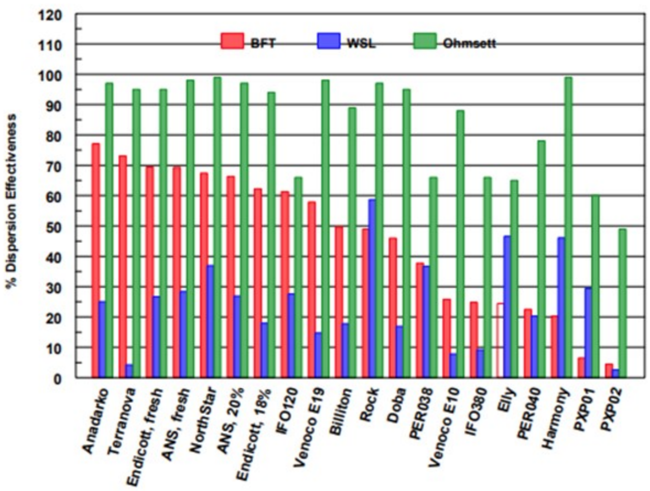

Figure 7. Synthesis of dispersant tests performed using various protocols (SL Ross Environmental Research, 2010)

Figure 7 demonstrates the variation in testing results when comparing bench-scale data (in small containers, no dilution, etc.) with mesocosm results. Mesocosm tests better approximate real-world conditions, but still have constraints. Several field trials have studied the effectiveness of surface dispersants in the open ocean. Reliance upon relevant modelling must continue to help us predict effectiveness of SSDI in future well blow-out events.

Dr. Jonas Gros from GEOMAR Helmholtz Centre for Ocean Research Kiel shifted the focus from surface dispersant use to subsea dispersant use with a presentation titled "Effect of dispersant on the behavior of petroleum in the deep sea during the DwH accident". The primary objective of subsea dispersant application was to reduce droplet size, thus decreasing the ascent speed and increasing the surface area to volume ratio of the oil, resulting in an increase in the extent of aqueous dissolution experienced by a range of petroleum compounds. At the blowout site, the oil and gas mixture escaped from the pipe, entraining ambient seawater. As this mixture rose, the seawater detrained developing a subsea hydrocarbon-rich intrusion containing dissolved hydrocarbons and microdroplets at 900-1300m. Larger oil droplets escaped the neutrally buoyant plume and ascended to the sea surface where the more volatile compounds rapidly evaporated into the atmosphere.

This sequence of events is confirmed by aircraft measurements collected during two flights (deGouw et al. 2011, Ryerson et al. 2012); one of which was used for model validation (Gros et al. 2017). Researchers used the VDROP-J model, which has been validated by field observations to predict the initial droplet (and bubble) size distributions (DSDs) (Zhao et al. 2014). Using these initial DSDs, the TAMOC (Texas A&M Oil Spill Calculator) model was used to simulate the oil and gas behavior and transport. The simulations predicted the independent behaviors of over 200 individual petroleum molecules and pseudo-components (Gros et al. 2016, 2017, 2020) Dr. Gros presented comparison data for three different scenarios: field data, model results with SSDI and model results without SSDI. The model predicted that SSDI led to a 26% increase in aqueous dissolution of petroleum compounds and a decrease in the atmospheric emission of the lighter compounds. Several VOCs such as the human-carcinogen benzene were particularly affected. SSDI did not significantly change the amount of heavy hydrocarbon compounds that reached the surface, but did decrease the VOCs that reached the surface by transferring their distribution to the deep-water intrusion and increased the amount of dissolved petroleum hydrocarbons in the upper water column.

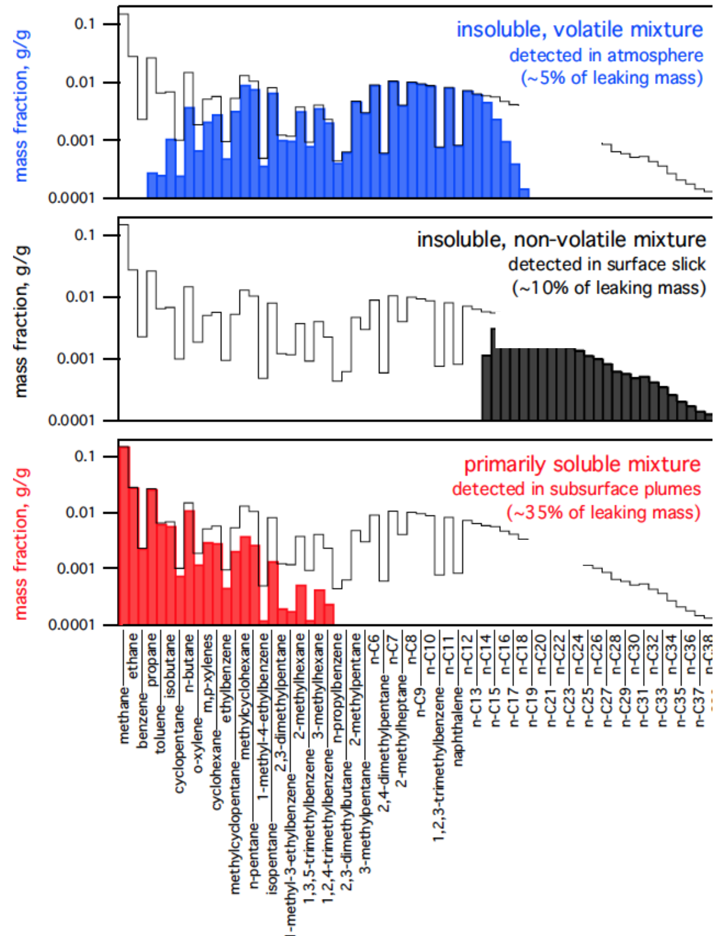

Figure 8 Composition of hydrocarbons in various regions and structures (evaporated, surface slick, and dissolved). (Ryerson et al. 2012, Copyright (2012) National Academy of Sciences)

The next presentation was given by Dr. Michael Schlüter from the Hamburg University of Technology, and the topic was “The Influence of Energy Dissipation Rate and Dispersants on particle Size Distribution”. The topic of interest here is what happens to the gas saturated oil (mimicking live oil) in this high pressure environment when it encounters a large decrease in pressure as in the pressure drop between the blowout preventer and the ambient water (almost 15 bars/s). By lowering the pressure, the saturation concentration of gas in oil is lowered, causing gas to appear within the oil. As the gas expands within the oil droplets, it causes the droplet to "explode" and creates this "cappuccino effect", i.e. the emulsification of oil, gas, and water. This process was mimicked in the high-pressure module, where an endoscope was deployed to measure droplet size distribution. The addition of "live oil" in the module increases the expansion angle and decreases the particle diameter. When dispersant is applied, no further decrease in droplet sizes is visually observed. This was verified by viewing the emulsification mixture under the microscope. Unfortunately, particle size distributions within the oil were unable to be measured in the high pressure laboratory. This has been done in additional experiments at the Technical University of Hamburg at Harburg (TUHH) macro-Jet setup. It could be confirmed and modeled, that with increasing turbulent kinetic energy, the droplet size is decreasing.

Q. *How can you tell based on oil properties which oils are dispersible and which are not? What would be the rule of thumb?* **A.** One can look at the API gravity, and if the number is in the upper 20s through 30s, it is dispersible. However, recent studies have indicated that oils with a much lower API can also be dispersible.
Q. *Where was droplet formation?* **A.** There likely was strong mixing within the BOP preventer.
Comment: It is too difficult to test all dispersant options in the lab or in mesocosms, and if there is a spill of opportunity, then we should apply them and see if they work. There are currently field kits to determine dispersibility that take about five minutes.
Comment: The droplet size distribution was different before and after the riser pipe was cut. Before it was cut there were many small holes the oil was escaping from, and this contributed to the small droplet formation.
A. This was simulated and the size of the kink holes didn't replicate the small droplets in the model. The kink holes were not small enough to generate enough volume of small droplets. The droplet size distribution can be pre-calculated by taking into account the energy dissipation rate.
Q. *Would this change what the responders do?*
Comment: For the response the solution is rather simple. The primary goal is to make the droplets small; that is the indicator of subsea effectiveness and the main concern of first responders. Although this may not change what the response it, it will inform modeling studies.
Comment: There is some disagreement about the 50 bar pressure drop at the BOP due to the geometry of the BOP. Also, smaller bubbles might have been due to the jagged pipe edge creating additional turbulence and not the pressure drop.
Comment: There was disagreement among attendees related to the field data used for model validation. Atmospheric data collected during the spill showed very little variation in evaporating hydrocarbon composition (Ryerson et al. 2012) between May and June and that the releases benzene was nearly completely contained to the water column and expressed minimal signature at the sea surface.

SESSION VIII: Oil vs Dispersed Oil Modeling Studies

Dr. Claire Paris from the University of Miami provided an introduction to this session that summarizes the modeling work for oil and dispersed oil. The primary goal for these modeling studies is to try and predict the transport, distribution and composition of oil, and these parameters change with the extent of saturation (GOR) and dispersant applied. From previous modeling work (Socolofsky and Adams 2005) it was demonstrated that a subsurface multiphase plume would form regardless of dispersant application due to the thermodynamic processes within the buoyant plume. The modeling effort is a Lagrangian based method that links the near and far field components through the DSD (Paris et al. 2012). The nearfield modeling encompasses the flow rate, gas to oil ratio (GOR), chemistry, equations of state, the pressure drop and the pipe geometry. The near and far field models are linked through oceanic conditions and other processes such as biodegradation, dissolution, sedimentation, surface evaporation and photooxidation (Figure 9).

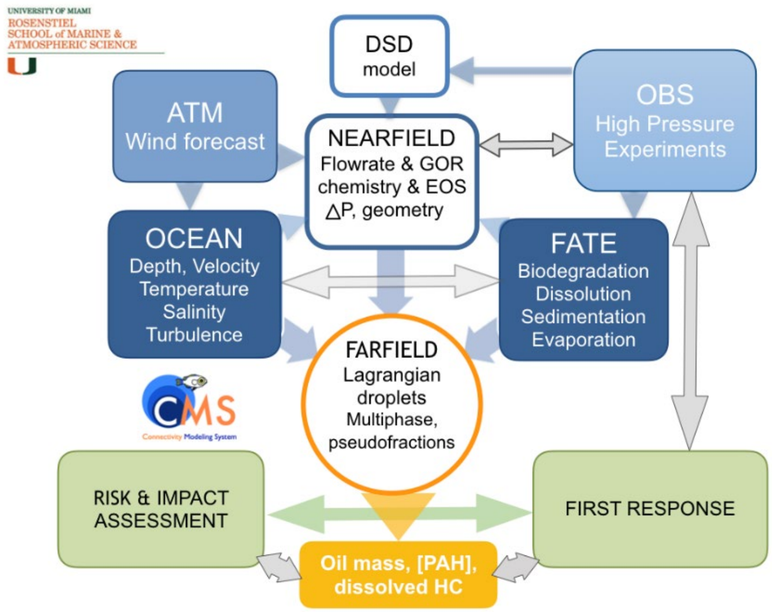

Figure 9. Near and far field model framework (Vaz et al. 2021)

To capture a full quantitative analysis of oil transport, the full three-dimensional model enhances understanding of the dynamics at the surface as well as the deep ocean and associated oil concentrations. The questions are: Where did the oil go, and how much? What was the effect of SSDI? In order to convert droplet trajectories into oil concentrations the model computes the concentration of oil in a layered ocean (Perlin et al. 2020). Different layers will have every changing quantities of oil (by mass), and these change with the use of SSDI. These differences may impact the response. Another approach is called the probability forecast, and it computes the probability of an area exceeding a certain TPH concentrations, and results in the probability of some threshold value in the model domain. These have no intrinsic value but can be used to calculate risk or weighing trade-offs. This method can be used to compute the probability for seafloor and coastal oiling. What goes into the model is the chemistry of the oil, composed of hydrocarbon pseudo-compounds. There is no limit to how many pseudo-compounds can be in the model; currently there are 19 (Vaz et al. 2019). These are single phase oil drops. It's noted that the initial condition for model initialization must have an accurate droplet size distribution (DSD, Faillettaz et al. 2021).

The next presentation by Dr. Michel Boufadel from New Jersey Institute of Technology discussed the near field model components, specifically the VDROP model and how it can be applied to oil jets in the VDROPJ version. He then discussed bubble and droplet formation associated with and without dispersants. VDROP considers oil in a controlled volume and interacting with turbulent eddies which are the break-up mechanism to form smaller droplets Subsequently, coalescence can occur and form larger oil droplets. Coalescence only occurs if the amount of oil in water is more than 30%. When oil only escapes from a "core" there are two sources for droplets; the shear layer and the core. The plume expands as it entrains water. In the VDROP model, at each vertical distance from the core, expansion is allowed, resulting in diluted oil. The energy dissipation rate and mixing energy decrease (Zhao et al. 2014; Boufadel et al. 2020).

The VDROPJ model was improved from experiments performed at the Bedford Institute of Oceanography in Canada. Alaskan oil with (DOR 1/20) and without dispersant was released from a 2.4 mm nozzle. The droplet sizes were measured (0 to 400 microns without dispersant) with an average 175 microns. The model was able to reproduce observations. With dispersant, the droplet sizes ranged from 2 to 38 microns with an average of about 10 micron and a bimodal distribution. The VDROPJ model with the version published in Zhao et al. (2014) was not able to reproduce the results in the tank. In the literature, dispersant applications in experiments both decrease droplet size and create bimodal size distribution. This may have been due to a process known as "tip-streaming", where oil sheds of droplets and creates very thin filaments of oil due to the inequitable distribution of dispersant surrounding an oil droplet. Tip streaming decreases with increasing viscosity and increases with increasing mixing energy. When tip streaming is incorporated into VDROPJ, model output for DSD becomes consistent with observations.

How and when to apply dispersants? When dispersant application is aiming for a DOR of 1:20, these numbers are set by the bulk properties of the oil. However, locally the DOR will not match the bulk properties. Tip streaming creates an inconsistently applied dispersant effect and is not a favorable outcome when responding to an oil spill. Additionally, the "puffy behavior" seen at the exit of the well head indicates that churn flow is occurring within the pipe before the oil and gas mixture is released. This is a phenomenon that needs additional investigation, however, discharge estimates and gas content measurements from DwH are consistent with a churn flow regime.

Dr. Michael Schlüter from the Hamburg University of Technology followed Dr. Boufadel with a presentation discussing the influence of oil degassing on droplet rising velocity. The droplet's rise velocity is part of the modeled nearfield processes, tracking the droplets as they rise in the water column. In Hamburg, the experimental designs in the mesoJETs were developed due to the difficulty associated with scaling down the blowout scenario, and experiments were performed at different scales to obtain the correct energy dissipation rate. The measured particle size distributions for these various experiments were compared to the Weber model as well as the TKE (Total Kinetic Energy) model. All of the resulting DSDs are log normal. For different size nozzle diameters, if the energy dissipation rate is adjusted by changing the outflow velocity, similar DSDs can be generated. Further, the Sauter number can be used to calculate mass transfer rates. When the Sauter mean diameter is compared to the maximum energy dissipation rate, the dissipation rate decreases and the droplet size increases. These findings are in good agreement with the model, and can be extrapolated to larger scales. However, when these are compared with the macrojet experiment with the larger nozzle size, the results deviate from prediction and result in smaller droplet size than predicted. This is due the droplets breaking up at certain dissipation rates and when we incorporate the pressure drop is incorporated, the theoretical Sauter diameter is consistent with the measured.

As the gas saturated droplet rises in the water column it may undergo internal degassing; as live oil rises, the pressure decreases and gas bubbles may grow within the droplet. The droplet diameter increases with decreasing pressure (as it ascends) and the rise velocity increases (Malone et al. 2018, Pesch 2020). The methane in the oil cannot dissolve into solution and the droplet expands. In Hamburg, an experimental setup was designed with a live oil droplet and a countercurrent flow that keeps the droplet in the same vertical location. The pressure is decreased to mimic the droplet rising and the droplet size increases. In this setup (methane-saturated oil at 6 MPa and a pressure decrease rate of 1 MPa/min), time corresponds to a certain rising height. This has been incorporated into the CMS model.

Dr. Paris resumed her presentation and discussed the degassing experiments and associated modelling efforts. The shape of the initial droplet size distribution is critical as it changes the rising time of the droplets. This is consistent with the VDROPJ model that shows rising time is longer due to the tip streaming. The various distributions found in the literature (Log normal, Rosin-Rammler distribution, and Gros et al. 2017) are incorporated into the 4-d model and compared to each other in terms of the resulting surfaced and sedimented oil distribution (Faillettaz et al. 2021). Most of the differences occurred in the amount of oil that surfaced using the RR distribution.

In a new degassing module of the oil-CMS model (Pesch et al. *submitted*), each droplet is composed of two phases and the fraction of gas must be specified. The modelling effort compared three different scenarios: (1) no degassing, (2) variable degassing, and (3) full degassing. There was not much difference in the droplet size distribution between full degassing and variable degassing. With no degassing the DSD changes over time and with variable degassing the droplet size distribution changes to bimodal over time. It is proposed that the changes in the amount of oil that came to the surface over time could have been due to degassing.

RECOMMENDATIONS:

- Both chemistry (GOR, saturation of the gaseous phase with oil aerosol and vice-versa) and physics (energy at the blowout, pressure-drop, turbulence dissipation rate (TDR)) are important for modeling transport and fate of oil and dispersed oil
- There has been much progress on understanding the initial DSD with laboratory upscaling jet-plume experiments, but more experiments need to be performed under high pressure conditions to augment the limited amount of experimental data.
- Necessary areas of research for both near-field and far-field modeling
    - evaluating the impact of gas and pressure-drop on DSD
    - evaluating the role of gas bubbles in scavenging dispersants
    - understanding the fundamental and dynamic nature of iDSD and their evolution to bimodal DSD

Much of the Q/A in this session was centered around what the model output was giving for the droplet sizes that eventually surfaced, and the concentration of methane in these droplets compared to what was measured in the field. The CMS model does allow for methane dissolution at depth. The droplet sizes that are surfacing are droplet sizes that are initially larger than 70 to 100 microns. Larger droplets would rise quickly in a matter of a few hours. During the ascent, biodegradation acts on the oil/gas, and to implement this in the model, oil pseudo-components (i.e. multi-phase and multi-fraction droplet) would need to be included. Modeling of pressure-induced degassing reveals a rapid evolution of initial DSD into a bimodal distribution and a shift to a larger mean droplet size. The faster rising velocity of the larger mode may lead to an increase of surface oil concentration.

During this session there was considerable discussion related to methane degassing within the plume and throughout the water column. At a pressure decrease rate of 1 bar/min, which is the closest to the field conditions, it was suggested that degassing would only occur when the pressure is close to atmospheric pressure. This indicates that droplet ebullition did not happen in the deep sea during the Deepwater Horizon blowout, according to simulations that included the effect of ambient methane concentrations (Gros et al. 2020). The volume of water in the plume was much larger than the volume of oil, such that most of the gas could aqueously dissolve. However, within the gas plume it is quite difficult to estimate the surrounding methane concentration. Furthermore, if bubble nuclei within the droplets exist at the well-head, which is quite likely, it was argued by some that the gas will not dissolve into the water column but diffuse into the bubble nuclei as they are both hydrophobic. An alternative hypothesis is that mass transfer in fact would occur both at the gas-oil interface and at the oil-water interface. Sauthoff et al. (2013) showed that substantial ebullition can happen during field experiments where a cylinder containing methane-saturated decane was transported upwards by a remotely operated vehicle. However, what happens to droplets will absolutely depend on their size, on the initial pressure at which they were saturated with methane, on their release depth, and on the pressure decrease rate. Valentine et al. (2010) showed a secondary methane intrusion layer at approximately 850 meters, indicating that methane rose above the first intrusion at 1000-1200 meters. Pressure-induced mass transfer may be a mechanism for the methane to expand the droplet, decreasing its average density while rising in the water column as per TUHH experiments (Pesch et al. 2018) and the multiphase (liquid oil and methane) droplet and oil spill model (Pesch et al. 2021). This is an area ripe for additional investigation.

SESSION IX: Effects of Dispersants on Microbes

The session on the impacts of dispersants on microbes included presentations by Dr. Roger Prince and Dr. Samantha Joye. Dr. Prince is a retired environmental microbiologist and chemist who was previously with Exxon Mobil and Dr. Joye is a microbiologist and professor from the University of Georgia.

Dr. Prince discussed the different characteristics that contribute to the effectiveness of microbial degradation of oil, dispersants, and dispersed oil. Generally speaking, microbes are the most important first responders to an oil spill. However, answering the questions related to how dispersants impact degradation is not trivial because it depends on the state of the oil. Oil slicks are relatively resistant to microbial degradation until or unless they become dispersed as small droplets. This can happen in storms without any intervention, but it does not happen in mild weather. Fortunately, the addition of dispersants allows the generation of small droplets with minimal wave energy and transforms a slick into an available food source which is subsequently biodegraded rapidly. Even in the presence of dispersants, oil slicks are difficult to biodegrade unless there is a source of physical energy, mostly contributed by wave action. In the absence of weather systems to physically disperse oil slicks, very little biodegradation occurs in long lived slicks and a slick will eventually reach the shore or beach, either as a "Black Tide" or as tarballs. Once oil reaches the beaches, biodegradation is slow due to the thickness of the oil and nutrient limitations at the shoreline. During the EVOS (Exxon Valdez oil spill), shorelines were mechanically washed of excess oil, followed by the addition of fertilizers to stimulate biodegradation. However, oil in its tarball state is long lived and degradation is very slow.

Dispersants are mixtures of both ionic and non-ionic detergents in a hydrocarbon solvent, all of which are "Generally Regarded As Safe" (GRAS). Corexit 9500, in particular, is the result of decades of research. Dispersants are difficult to measure and quantify in the field and when they are used for oil spill response, their application is used in relatively very small volumes, at the equivalent of one teaspoon per square meter. This quantity is further diluted as the surface application is incorporated into the sea. Two research groups (McFarlin et al. 2018 and Brakstad et al. 2018) have documented the rate at which the components in Corexit 9500 biodegrade. The components of interest in dispersant are: (1) DOSS – with half-lives ranging between 4 and 24 days, (2) Span-80, with half lives of 20 days, and (3) Tween 80 and 85 with half-lives between 3 and 20 days. All of the surfactants are found elsewhere in the US consumer market, especially in cosmetics and over-the-counter medications. During dispersant application in response to a spill, dilution quickly occurs, and oil and dispersant concentrations at the site of application fall to only a few ppm after a couple of hours. Because oil is characteristically insoluble, there are two defined environmental pathways: floating slicks and dispersed oil. Slicks have a small surface to volume ratio and are not significantly acted upon by microbes, although they are subject to photo-oxidation and emulsification. Dispersed oil entrains in the water column at depths where evaporation and photo-oxidation are minimal and the large surface to volume ratio encourages significant microbial degradation. The application of dispersants simply lowers the amount of mechanical energy required to produce drops from slicks. If enough mechanical energy is available, dispersants are unnecessary.

Various groups that have looked at the biodegradation of oil in the plume after the DwH blowout all determined that a significant portion of the oil is acted upon and degraded within a few weeks. Dr. Prince presented a table of studies that looked at the biodegradation rates of various types of dispersed oils (varying oil and different dispersants) at a range of temperatures (Table 2). These are for oils that are in dispersed droplet form. Oil that has weathered and washed ashore is much thicker and biodegradation is slow. In the water column, as biodegradation occurs, the oil droplets become enriched in the heavier molecules and the droplet sinks. Of the 80% that is biodegraded, about 50% of it is converted to microbial biomass and 50% is converted to CO_2.

Dr. Samantha Joye provided the next presentation that summarized the role that microbial fitness plays in the biodegradation of oil. Dr. Joye began her time by noting that there is evidence in the peer-reviewed literature of sustained deposition of contaminants to the seafloor (Yan et al. 2016). The term fitness for the following summary is defined as the ability for an organism to survive and reproduce in the environment in which they find themselves. Because microbial organisms can instantaneously respond to environmental cures, they play a significant role biodegradation. However, there are complex biological processes and interactions in play that regulate and impact biodegradation.

To obtain insight into microbial fitness, the behavior of two dominant organisms was investigated, *Marinobacter* and *Colwellia* and it was found that the response to oil and dispersants is species specific. The experiments were performed on a roller table to mimic the movements that organisms undergo in the field both in surface slicks and in the subsurface plume. The *Marinobacter* responded well to the oil-only treatment but were inhibited by the presence of dispersants; alternatively, *Colwellia* responded strongly in treatments that had dispersants and less-so in treatments with oil-only. Sequenced genomes were taken and all core genes and accessory genes were identified. It was found that *Marinobacter* exhibited a classic oil-degrader response at the species level, showing a response in the accessory genes. However, *Colwellia*, showed signs of being an opportunistic oil-degrader. This study shows that some organisms are well suited to respond to oil if dispersants are added, and there are others that might be more effective oil-degraders in the absence of dispersants. (Peña-Montenegro et al. 2020; Peña-Montenegro et al. in review a). Evidence also was found that the microbial community changes gene expression in varying exposure regimes. (Peña-Montenegro et al. 2020; Peña-Montenegro et al. in review b).

To determine the role that fitness plays in degradation inside the plume, *Marinobacter* TT1 was isolated from the plume and grown under starved and well-fed conditions. Both cultures were transferred to a hexadecane-rich medium and exposed to dispersants. In the treatments with limited food sources, the presence of Corexit reduced *Marinobacter* growth but not in the well-fed cultures. This is of particular relevance for field conditions because the starvation conditions are representative of oligotrophic ocean. These organisms are less adept at degrading oil in presence of Corexit if they are not at optimal fitness before exposure (Rughöft et al. 2020).

Table 2 Summary of studies that investigate biodegradation of various oils. Full citations are found in references.

Component Measured	Oil Type	Half-life days	Seawater inoculum	Temp.	Dispersant	Citation
Total GC-detectable hydrocarbon	Alaska North Slope crude oil	14	NJ, USA	8°C	None	Prince et al., 2013
		11		8°C	Corexit 9500[1]	
		7		21°C	Corexit 9500[1]	Prince and Butler. 2014
		36	Barrow, AK, USA	-1°C	none	McFarlin et al., 2014
		37		-1°C	Corexit 9500[1]	
	Macondo crude oil	26	Trondheimsfjord, Norway	5°C	Corexit 9500[2]	Brakstad et al., 2015
		11	Gulf of Mexico, USA	5°C	Corexit 9500[2]	Wang et al., 2016
	Alaska North Slope crude oil	7	NJ, USA	20°C	Corexit 9500[2]	Prince et al., 2016a
		7		20°C	Slickgone NS[1]	
		7		20°C	Finasol OSR52[1]	
	European crude oil	13	Logy Bay, Canada	5°C	Corexit 9500[3]	Prince et al., 2016b
		10	NJ, USA	21°C	Corexit 9500[3]	Prince et al., 2017
	Bintulu crude oil	28	Penang, Malaysia	26°C	none	Zahed et al., 2010
		15		26°C	Corexit 9500[1]	
Total alkanes	Macondo crude oil	~3	Gulf of Mexico, USA+ high oil and nutrients	25°C	none	Olson et al., 2017
		~3		25°C	Corexit 9500[1]	
	Statfjord C crude oil	9	Trondheimsfjord, Norway	5°C	none	Brakstad et al., 2018
		9		5°C	Slickgone NS[3]	
		12		5°C	Slickgone NS[4]	
		10		5°C	Slickgone NS[5]	
	Grane crude oil	10		5°C	Corexit 9500[3]	Ribicic et al., 2018
		5		13°C	Corexit 9500[3]	
	Troll crude oil	17		5°C	Corexit 9500[3]	
		7		13°C	Corexit 9500[3]	
		25	Artificial + enrichment	5°C	none	Zhuang et al., 2016
		9		5°C	JD-2000[4]	

The experiments to determine the effects of nutrient availability on biodegradation behavior in the surface waters were only run for a couple of days due to the short live span of oil slicks. The experiments were performed in the dark to eliminate any contributions from phytoplankton. Increase in bacterial production occurred with nutrient addition. *Marinobacter* and *Alcanivorax* flourished in treatments of oil and oil/dispersant mixtures with no nutrient stress, but it was *Alteromonas t*hat was able to grow strongly with oil and *Corexit* even with nutrient stress.
In assessing the role of microbes in oil and dispersed oil biodegradation, one must consider the role of fitness. Without considering environmental interactions while interpreting post-spill field data, the holistic picture of the efficacy of microbes is missed. The associations in the environmental system indicate that it is primed to break down oil but there are factors that could limit the capability of microorganisms to do so.

Q. *Do the conditions in the roller table really mimic plume conditions?* **A.** Yes, even though dilution does occur in the field, the plume did stay together and limited dilution. The plume was like a "snake in the field". Laboratory conditions also matched concentrations of hydrocarbons and DOSS in the field. The plume was sampled daily for six weeks, and the concentrations in oil and DOSS that were developed in the laboratory were found approximately 12 km southeast of the well head, which corresponds to approximately 10-day post release. Also, the concentrations for the laboratory experiments were consistent with those found by Wade et al. (2011).
Q. *Does the dispersant-only treatment provide any real-world relevance?* **A.** Because the real-world is nutrient-limited, the dispersant alone treatment is an important carbon cocktail. It also provided the conditions to be able to say that the dispersant is driving the community shift more than the oil is. The dispersant-only exposures were created more to be able to disentangle the microbiological response.
Comment: Dissolved dispersants would actually appear in the environment since dispersant leeches quickly from oil droplets. See Riehm and McCormick (2014) and Hansen (2017).
Q. *What about the role of phytoplankton?* **A.** There are interesting associations that occur between phytoplankton and hydrocarbon degraders. Phytoplankton provide micro-niches for certain microbes. The role of fungi is also really exciting.
Comment: Microbes from the deep sea are at low temperatures and are slightly easier to manage. However, for experiments using surface microbes, conditions are more complicated. Those microbes are stressed due to UV, viral dynamics, nutrient stress and kinetics in how they fight for nutrients.
Comment: Sedimentation alone provides a significant impact to benthic community, and any oil in the sediment is just insult to injury.

SESSION X: Population Level Impacts of Dispersants and Dispersed Oil

The main focus of session ten was to discuss how to translate individual organismal impacts into population level effects. Dr. Joel Fodrie from the University of North Carolina at Chapel Hill discussed changes in nearshore and estuarine fish species post DwH, and Dr. Nathan Putnam from LGL Ecological Research Associates Inc. discussed changes in the commercially important Red snapper populations. Dr. Robyn Conmy from the Environmental Protection Agency moderated the session.

The focus of Dr. Fodrie's presentation centered around the impacts of oiled environments in the nearshore on fish populations. There is difficulty in teasing out the effects of dispersants and oil, and the summary was tuned to discuss various exposure vectors and associated impacts: genomic expression, larval and juvenile damage, habitat loss, phytoplankton and food web impact (Figure 10).

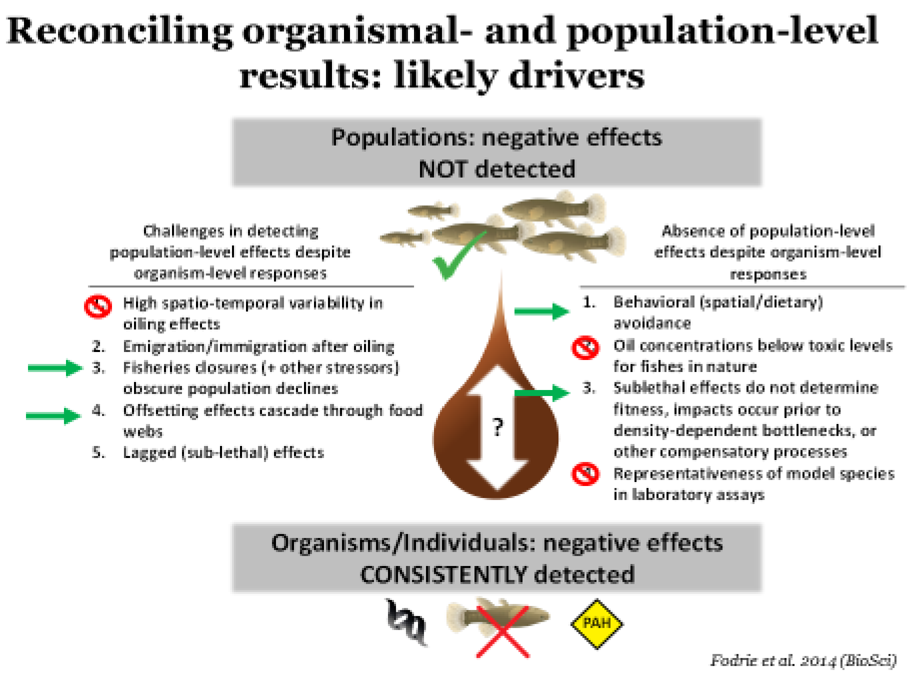

Figure 10. Potential mechanisms for the contrasting results of organismal (genomic, physiological, developmental) and population-level (densities, assemblage structure) investigations detailing the responses of fishes to the 2010 Macondo oil spill. (Fodrie et al. 2014).

Fodrie et al. (2014) summarized the post-DwH laboratory exposure studies on individual organisms. Consistent negative impacts were found in the individual estuarine and nearshore fishes that were sampled in the field from oil-impacted areas or assayed in controlled laboratory exposure trials (Table 3). For instance, Gulf killifish were sampled in the impacted and non-impacted marshes in Louisiana, Mississippi and Alabama before, during and after oiling from the DwH spill. Decreasing gill function was found in the oiled marshes from May to September of

2010 (Whitehead et al. 2012). Offshore species were also sampled for impacts and researchers found evidence of oil exposure in yellowfin tuna, such as deformed heart development, eye, and spinal column (Incardona et al. 2014). While these individual-level effects are significant, a remaining question is whether these injuries exert influence on population-level abundances and community dynamics.

Table 3. Catalog of studies examining the organismal responses of estuarine fishes to GoM oil pollution. (Fodrie et al. 2014)

Citation	Oil-Spill Context	Organism	Lab or Field	Collection Locations	Genomic Response	Physiological Response	Morphological Defects	Increased Mortality	Population-level (fitness) Impacts Considered
Ernst et al. 1977	*No. 2 Fuel Oil*	*Fundulus grandis*	Lab	TX	n/a	Y	n/a	Y	Presumed Negative, Not Explicitly Stated
Fucik et al. 1995	*Generic Oil + COREXIT*	*Atherinopsidae, Clupeidae, Sciaenidae*	Lab	Western Gulf and Atlantic	n/a	n/a	n/a	Y	Presumed Negative, Not Explicitly Stated
Gregg et al. 1997	*Diesel-fouled sediments*	*Gobionellus boleosoma*	Lab	LA		Reduced feeding			Not Indicated
Whitehead et al. 2012	*Macondo*	*Fundulus grandis*	Field	LA, MS, AL	Y	Y	n/a	n/a	Expected Negative
de Soysa et al. 2012	*Macondo*	*Danio rerio* (embryos)	Lab	n/a	n/a	n/a	Y	n/a	Presumed Negative, Not Explicitly Stated
Garcia et al. 2012	*Macondo*	*Fundulus grandis*	Field	LA, MS, AL	Y	n/a	n/a	n/a	Presumed Negative, Not Explicitly Stated
Dubansky et al. 2013	*Macondo*	*Fundulus grandis* (adults and embryos)	Lab and Field	TX, LA, MS, AL, FL	Y	Y	Y	n/a	Expected Negative
Incardona et al. 2013	*Macondo*	*Danio rerio* (embryos)	Lab	n/a	Y	n/a	Y	n/a	Presumed Negative, Not Explicitly Stated
Kuhl et al. 2013	*Macondo* + COREXIT	*Fundulus grandis*	Lab	n/a	n/a	n/a	n/a	Y	Presumed Negative, Not Explicitly Stated
Crowe et al. 2014	*Macondo*	*Fundulus grandis*	Lab	n/a	Y	Y	n/a	n/a	Presumed Negative, Not Explicitly Stated

In the peer-reviewed literature, population and assemblage level studies were summarized and practically all studies show an increase in catch rates and community-level stability post-DwH. Despite known injuries at the organismal level, catch rates of juvenile fishes (Fodrie and Heck 2011, Able et al. 2015, Schaefer et al. 2016, Martin et al. 2020) and decapod crustaceans (Moody et al. 2013, van der Ham and de Mutsert 2014, Grey et al. 2015) in nursery environments, such as seagrass meadows and salt marshes, of the northern Gulf of Mexico (Louisiana to Florida Panhandle) were higher after the DwH spill relative to the years before the catastrophe. Similarly, SEAMAP data (2000-2018) from the nearshore region (0-3 miles offshore) of the northern Gulf of Mexico also showed an increase in catch rates in the years immediately after DwH (Martin et al. 2020). This corresponded with a decrease in species diversity as a few species (e.g., Atlantic croaker) dominated catches during 2010-2011.

In the literature, we see evidence of organismal costs from oil exposure, however the population level studies do not show similar results (Fodrie et al. 2014). How can these two results be reconciled? In fact, the population is undergoing a complex perturbation, and the increase in catch rates is indicative of some instability. Some possible explanations for this perturbation are fishery closures or the offsetting of predators (Figure 10). Alternatively, the resilience of the estuarine-dependent fishes may be due to a portfolio effect of multiple semi-independent but connected breeding populations compensating for those potentially affected. It's evident that whatever the mechanism, fish at population levels have compensatory dynamics. These dynamics that potentially contribute to an uptick in fishery population have also been shown to occur in the Grand Banks (Levy and Lee 1988).

The next presentation was given by Dr. Nathan Putman and reviewed research specifically related to Red Snapper. The discussion focused research efforts related to modeling various spill scenarios and assessing the actual and projected impacts of the DwH spill and potential future spills on eggs and larvae, and translating this information into population-level impacts. Because Red Snapper are an extremely commercially relevant species, much is known about their life histories (SEDAR, 2018). The egg and larvae stages are highly susceptible to perturbations, mostly due to their inability to avoid potentially hazardous environments. It was estimated that about 4 billion larvae were lost during the DwH spill, translating to approximately 112,000 kg of Red Snapper adults, which is approximately 2.2% of the population. What if a spill occurred on the shelf? How much does spill location contribute to the fishery impact? A risk analysis model was used to determine the distribution and location of water parcels that contained lethal concentrations of oil. The modeled spill occurred on July 15th coinciding with the spawning time for Red Snapper. The 225,000 bbl spill lasted for over 5 days and simulations were run with and without dispersant application. The spills and impacts were modeled using the SIMAP physical fate/biological effects model (French-McCay 2004, 2009). A bold exposure regime was used with threshold levels that killed 50% of the test larvae when exposed for 96 hours. Egg and larval densities were used from the SEAMAP and CPUE data.

The ability to model population level impacts on Red Snapper is directly related to how much is known about their life history. Red Snapper is a long lived fish, with many reaching ages of over 50 years. Females over the age of 5 years produce anywhere from 10 to 88 million eggs per season during the peak spawning season, occurring from June to August. Red Snapper eggs have a duration of one day and a mortality rate of 0.5 (Gallaway et al. 2007, 2009). Red Snapper recruitment does not change much except under scenarios of a severe reduction in stock size, as noted by its high steepness parameter. This is shown by the modeled scenarios; even by choosing the worst case parameters, by assuming a one-hour exposure to a TPAH concentration of 1 ug/l over 350 to 500 square kilometers only resulted in an egg loss of about .06% of the total. Spawning data indicate that these could be replaced by a relatively small number of females, anywhere from 1 to 9%. Due to the steepness factor, it is projected that stock reductions would need to be quite large, reaching 84% before a reduction in recruitment would be expected. Red Snapper recruitment showed only showed a moderate decline indicating that the DwH spill did not impact the Red Snapper fishery and it appears healthy (Gallaway et al. 2020a, b).
Q. *Is the increase in CPUE a biomass issue?* **A.** For fish, we took length. Harvest weights did not change significantly.
Q. *Is it possible to separate out dispersed oil vs oil?* **A.** These are difficult to tease out. Fishery response to oil spills is normally quite resilient. In this model we are assuming that very bad things happen to individuals, but that there’s no significant impact on the population.

SESSION XI: Human Health Routes of Dispersant Exposure

GoMRI's investments in investigating the impact of oil and dispersant exposure on ecosystem extended to human impacts. Human health exposure begins with assessing the compounds and concentrations of hydrocarbons in the atmosphere that can make their way to the human population. Dr. Joseph Katz from Johns Hopkins University presented information on the dynamics at the air/sea interface that can allow for hydrocarbon exposure. Following was Dr. Paul Nony from CTEH (Center for Toxicology and Environmental Health) who presented the factors involved in assessing response worker exposure routes.

Dr. Katz's presentation "On the effect of dispersants on the aerosolization of oil" summarized some of the major studies performed dealing with oil droplets at the air/sea interface that aimed to: measure and model the breakup of crude oil into subsurface and airborne droplets, measure and model droplet size distributions, measure the transport of these droplets, and to investigate and characterize the oil/water interactions.

In the laboratory wave tank studies, oil and dispersant was added to the tank and wave energy was introduced. For scenarios with and without dispersant, droplet size distributions were measured at the surface. In the case with dispersant added, smaller droplets were generated and oil threads are formed (tip streaming) (Li et al., 2017). This was described in Session 8. Smaller droplet diameters would have likely been measured as the minimal droplet diameter is a function of the detection limit of the instrumentation. Further investigations looked at the aerosolization of oil, focusing on nanodroplets, (Afshar-Mohajer et al. 2018a, b). The addition of dispersants resulted in a massive increase in concentrations of aerosolized nanodroplets (oil + dispersant + wave energy). Volatile compounds released from the oil were measured during experiments, and a significant decrease in VOCs was found above the water's surface (hexane, etc.) but coincided with an increase in the concentration of nanoparticles.

During wave breaking, air bubbles are entrained in the surface layer, ultimately rising and bursting on the surface. Laboratory experiments were performed to investigate how bubble bursting can generate aerosols. The addition of dispersants in the presence of large bubbles (0.5 to 0.8 mm in diameter) increases the concentration of nanodroplets above the water's surface significantly, however, small and medium sized bubbles (0.1 to 0.4mm) even with the addition of dispersants did not show similar results. The mechanism contributing to this is that the larger bubbles break the film around the oil droplets. Nanoaerosol concentrations in the air for large bubble injection were much larger in laboratory air than in hepa-filtered air.

To determine the health risks associated with potential exposure to these nanoaerosols, it is important to look at their composition. What is the oil fraction in these nanoaerosols (Afshar-Mohajer et al. 2020)?. For these studies, dodecane was used as an indicator for crude oil and 1-(-2butoxy-1-methylethoxy)-2-propanol (BMEP) for dispersant. Laboratory results showed that the addition of dispersants increases the amount of oil in the airborne particles. Similar experiments were performed for weathered oil. The first compounds removed from oil are the most volatile compounds. However, in all cases, there is an increase in the aerosol concentrations above the air/sea interface, regardless of the weathering stage. Oil properties did influence the particle count. As oil viscosity increases, the particle count decreases. However, if the volatile components are removed, (ie. weathered oil), the number of nanoparticles increases.

This information on the concentrations of oil at the air/sea interface is important to assess human exposure, which is of critical importance during the response process. Dr. Nony discussed the possible exposure routes to response workers, and summarized the mitigation strategies. Concern for workers during the response includes possible exposure to dispersants, particulate matter from controlled burns, vapors from crude oil and oil mist, cleaners, and other gasses like methane or hydrogen sulfide. There are three main routes for exposure: direct contact, ingestion, and inhalation. Most of the concern is associated with the inhalation of the volatile components. For the dispersant exposure concern, this could occur at the decontaminant station where equipment is cleaned, during the skimming operation, during the actual application, and during the loading of dispersant on planes.

During DwH, risk communication around central command lagged behind the news cycle with allegations that dispersants were banned, toxic, and not fully understood. The objective became to embark on a dispersant hazard communication mission with the workers to help them understand the safety of the chemicals and to demystify the process. In response to allegations of the possibility of people being sprayed directly with dispersants from a plane, an effort was made to disentangle myths from facts. The facts about aerial dispersant use:

- Aerial dispersants were applied from a height of about 75 feet above the water, in a swath approximately 150 feet wide, and at a rate of 5 gallons per acre.
- Spray nozzles on the planes were set for a droplet size 300-500 microns (a human hair is ~100 microns).
- Spray equipment was calibrated and tested by operations personnel.
- Aerial spraying of dispersants did not occur in the zone of simultaneous operations around the source.
    3 nautical mile (nm) setback from marine wildlife,
    2 nm setback from boats and platforms
- All aerial dispersant operations ceased on July 19, 2010.

Much effort was applied to the dissemination of publicly available exposure data and analysis on both volatiles and dispersants. The following list is not comprehensive, but provides an initial assessment of what is currently available.

- GoMRI GRIIC
  184,709 records; April 2010-January 2012

- NIOSH
  2577 records; June-August 2010
- OSHA
  4538 records; June-September 2010
- USCG
  1192 records; June-July 2010

Analysis

- Merged databases and filtered for target analytes
- Removed field blanks and sample records with missing information

Measurements on the concentrations of volatiles began on the 2nd day of response, but dispersant concentrations in the air were not measured until concerns were vocalized. Detection instruments were placed on industrial hygiene strike team members, specifically looking for BTEX compounds, 2-butoxyethanol and propylene glycol analytes which are the representative compounds of dispersant. An average detection of 0.1ppm/.05ppm was established for 2-butoxyethanol/propylene glycol, respectively, but was well below any occupational exposure values of 50 ppm/4ppm.

For future response scenarios, proper communication to the work force and to public stakeholders is critical regarding the actual and perceived effects of dispersants on the environment and to public health.

Q. *Did the submicron droplet concentration increase with dispersant application?* **A.** These droplets remained in the atmosphere indefinitely, and this was confirmed by what NOAA observed (Middlebrook et al. 2012).
Q. *Do these nanodroplets interact with our lung tissues*? **A.** This is an area of research that needs to be captured as a high priority.
Q. *Does the mass fraction of oil in the nanodroplets contribute to the human health risk*? **A.** Readers are referred to the study by Afshar-Mohajer et al. (2018a, b). They found that the application of dispersant reduced VOC concentrations by 1.6 to 3.34 times. However, the dispersant increased the nanoparticles by six times. This is very near to the source and does not take into account dilution. Also, this is still well below the health risk threshold.
Q. *Are there any data on exposure to the general public to dispersants?* **A.** Agencies were monitoring air at 5000 locations per day from Texas to Florida, looking for VOCs, fine particulate matter, and other combustion by-products. Low levels of these parameters were found close to the response site, so there was no need to monitor those elsewhere. There were no significant measurements of hydrocarbon byproducts in all locations.
Q. *What is the mechanism for the increase in nanodroplets*? **A.** This is just a speculation, but the surfactants may coat bubbles, inhibiting further gas diffusion.

Q. *What are the advances you would recommend for PPE?* **A.** First the industry needs to overcome challenges in real time monitoring techniques. There are portable hand-held GCMS that can take samples over a minute and provide speciated results at lower detection limits. This is an area of study where academia can contribute.

Q. *If we had the NRDA data or data that were caught in litigation earlier, how would that have changed the scientific projects moving forward*? This question was not fully addressed and put on the agenda for Friday.

SESSION XII: Dispersant Use in Frontier Areas

As industry explores drilling operations in frontier areas, workshop organizers prioritized this session to identify where contemporary research on dispersants through GoMRI can inform future research. Dr. Nancy Kinner from the University of New Hampshire's Coastal Response Research Center (CRRC) and Center for Spills in the Environment moderated the session. Doug Helton from NOAA's Office of Response and Restoration focused on potential dispersant use in atypical places like Alaska and the Arctic regions.

The primary question needing to be answered in considering dispersant use in these regions is are they worth the trade-offs (Figure 11)? Responders have experience in assessing various response technologies in temperate regions, but not as much in the Arctic. Many of these questions initially arose from Shell's campaign to search for oil in the Chukchi Sea, but also due to increased vessel traffic in the Arctic over the last 10 years. In Alaska, the dispersant pre-authorization plan in effect during the Exxon Valdez spill expired in 2008. 1n 2016, the Alaska Regional Response Team (ARRT) established a new, much more conservative dispersant use policy that includes a preauthorization area and an enhanced protocol for use of chemical dispersant during responses to spills of crude oil in western and central Alaska.

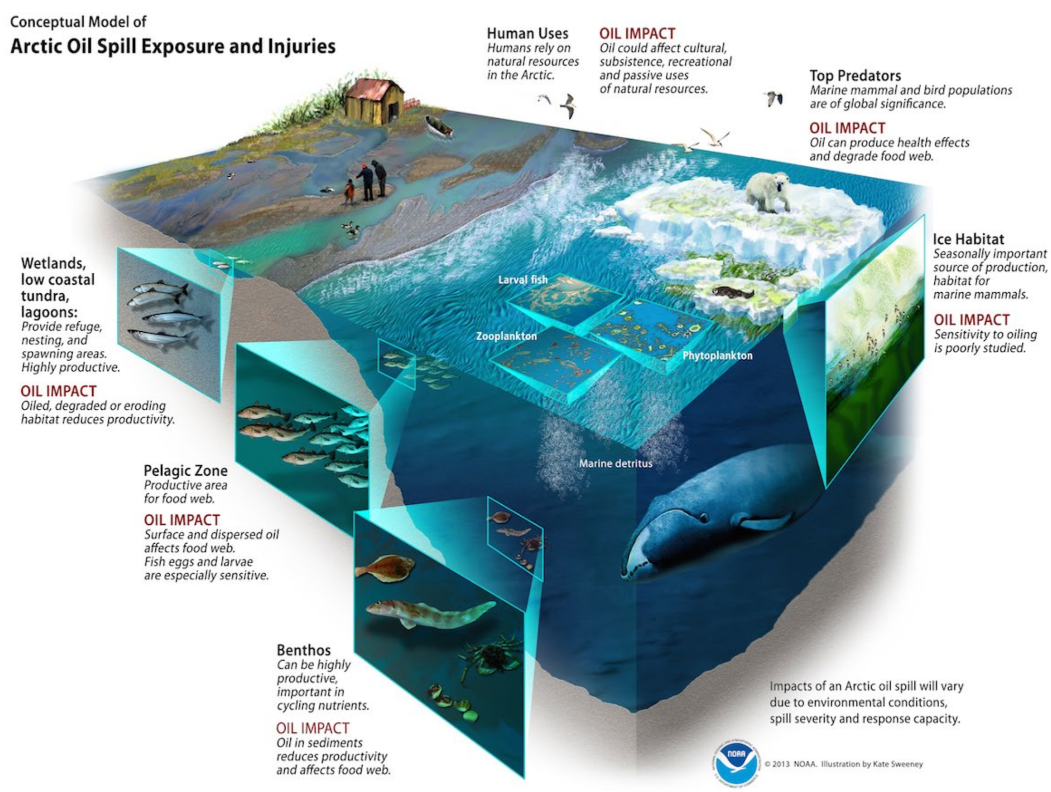

Figure 11. Considerations for ecosystem damage during Arctic oil spills. (Kate Sweeney, National Oceanic and Atmospheric Administration. Used with permission. Originally obtained from https://usresponserestoration.wordpress.com/2011/05/11/arctic-oil-spills/)

Many scientific and policy questions still exist for Arctic dispersants in U.S. waters. One of the outcomes of an Arctic oil spill drill for senior federal agency leadership identified the need for a definitive evaluation of the state-of-science of dispersants and dispersed oil (DDO), particularly as it applies to Arctic waters. To address this need, the CRRC coordinated a discussion among scientists with dispersant research expertise, as well as those with Arctic expertise, to determine the state-of-science (knowns and uncertainties) regarding DDO, as it applies to Arctic waters. Separate panels of scientists were convened to focus on each of the following topics concerning DDO:

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

The overall take-home message is that there is a large body of information about certain types of dispersants in temperate regions, but less research and information in the arctic.
Some things to consider that make the Arctic region a challenging place for conventional response options are the weather and presence of ice, the logistics associated with limited infrastructure, and the time and distance conventional response options would take to travel to the spill site would be significantly greater. These factors would make mechanical recovery of oil quite difficult.

However, for dispersants to be effective, application needs to occur on fresh oil and aircraft need good visibility to operate safely. Additionally as mentioned in Session IIa, dispersants don't work well in calm conditions and wave and sea surface mixing energy is needed. But the biggest concern is that dispersants, unlike mechanical response, do not remove oil from the environment. There are few case histories of dispersants use in the Arctic.

Because dispersants need to be applied on fresh oil to be effective, the decision to use them needs to be made quickly, within hours. One helpful reality is that oil weathers more slowly in the Arctic, extending the window slightly for dispersant application. Most areas of the US have some level of preauthorization to use dispersant. This is the case in Alaska as well, but there are many restrictions.

The CRRC state of the science review effort looked at questions relating to the efficacy of dispersant use in the Arctic and the potential tradeoffs that would need to be considered. The exercise was mainly a peer-review process. Logistical and operational issues were not considered, though they would be significant in the Arctic.

The hierarchy of questions that need to be addressed are:
(1) Will the dispersants work in the Arctic? Viscosity, temperature and wave energy are all factors for dispersant use. Increased viscosity, calm conditions caused by ice presence would inhibit dispersal (Trudel et al. 2010).
(2) Where will the dispersed oil go? In open water with less than 30% ice coverage, the oil and ice move independently of one another, and in areas of 80% or greater of ice coverage, oil moves with ice. Oil can freeze into ice and be transported (Afenyo et al. 2015).
(3) What's the fate of the oil? If oil is not dispersed in place, it may be deposited on the shoreline where it can persist for a long time. Decreased temperatures contribute to the slow degradation of many compounds, slower than in temperate conditions (McFarlin et al. 2014).
(4) What are the impacts on food webs and other animals? The Arctic regions have a prolific and critical sea life ecosystem that contributes to the productivity of the fisheries. This is one of the more difficult topics because less is known about Arctic food webs than others. In other regions, the priority for response is to protect the shoreline. However, this may not be as true in Alaska. The shorelines in this region experience ice scouring for much of the year decreasing the amount biota there. It is the offshore areas that are more productive (whales, walruses) and this may include the offshore shoal areas (Gardiner et al. 2013).
(5) What are the public health and food safety concerns? In Alaska in particular the human health implications would be substantial because of the subsistence fishery. The review revealed that less than 1% of the existing literature on oil and dispersants focuses on human health. Of the studies, many of them discussed concerns about responder health offshore. But there is also a health concern for those response workers at sea and cleaning shorelines even if dispersants are not used. In addition, the Arctic region poses unique challenges to address exposure from seafood consumption; 13% of the region's diet is composed of marine mammals. Due to the lipid richness of marine mammal tissue, this could pose a significant health risk due to biomagnification of oil compounds. This is a difficult risk communication challenge.
A more comprehensive summary for each of the above concerns is available on UNH's CRRC website and the reader may refer to the list below or visit: https://crrc.unh.edu/dispersant_science

Efficacy and Effectiveness	https://scholars.unh.edu/crrc/1/
Physical Transport and Chemical Behavior	https://scholars.unh.edu/crrc/4/
Degradation and Fate	https://scholars.unh.edu/crrc/3/
Eco-Toxicity and Sublethal Impacts	https://scholars.unh.edu/crrc/2/
Public Health and Food Safety	https://scholars.unh.edu/crrc/22/

Comment: The human health concern is not just related to seafood consumption, but factors contributing to stress must also be considered, and this includes misunderstandings about dispersants. What makes some communities more susceptible to disasters that can trigger food source loss or job loss?
Comment: In terms of shoreline impact, this can be a region that is critical for medicinal resources, and these must be prioritized during the exercise. **Response:** This was considered by

the Alaska RRT and the recently developed food safety annex to the Alaska oil spill response plans is quite broad and included resources used for medicine and culture.

Q. *What monitoring activities in these areas would be recommended and what improvements to SMART protocol are necessary? How can the academic community provide support in these areas?* **A.** The food safety issue is driven largely by NOAA and the State of Alaska to identify those resources, but questions still remain in terms of sampling. For example, in the case of the food safety annex, how much sampling should be paid for by the agencies vs the National Pollution Fund Center? As far as the SMART protocol, there are some unrealistic expectations due to scale of Alaskan shorelines and EEZ.

Comment: While dispersant use may be the best option given all of the tradeoffs, the community needs to be prepared for significant public backlash in terms of dispersant use. If dispersant use is agreed upon as the best response option, this will not be a "magic bullet". However, there are downsides to not dispersing the oil such as its longer-term persistence in the environment. Alaskans are well aware that oil that is not dispersed may linger in certain types of sheltered shoreline habitats. Thirty years later there are still oiled areas of Prince William Sound.

Q. *Can you comment on using the SMART protocol in these remote locations?* **A.** SMART protocols help responders determine the efficacy of dispersants (i.e., are they working as intended. But the ultimate question to answer, "are dispersants worth using?" is not the outcome of the SMART protocol. It does not provide an adequate set of protocols to answer that question, especially in the real time scenario. Measuring biological endpoints, for example, is difficult when the operational window to use dispersants is a matter of hours to days.

<u>SESSION XIII: Dispersants: Human Dimensions and Evolving Concerns</u>

The human dimension in the context of summarizing the impacts of dispersant use is complex and the previous two sessions presented data and/or scenarios that support this. The next session on the agenda faced this topic head-on, and was moderated by Dr. Helena Solo-Gabriele from the University of Miami with a presentation provided by the Gulf of Mexico Sea Grant extension specialists given by Drs. Missy Partyka and Emily Maung-Douglass. What are communities most concerned with when it comes to dispersant use? And how are these concerns addressed and communicated to serve a diverse group of stakeholders?

Since 2014, the SeaGrant team organized and facilitated over 60 group meetings to identify which topics related to oil spills remain a concern to affected communities. The main charge of the oil spill science extension specialists was to solicit input from various stakeholders around the Gulf of Mexico related to oil spills and to foster two-way engagement that address and respond to concerns. Dispersants *remain one of the most discussed* topics during these two-way engagement sessions. The questions and concerns were mostly related to their impacts on human health, atmospheric transport and the ultimate fate and toxicity. It is in this last item of concern that the SeaGrant team assigned significant effort. During the Q&A sessions, attendees of the meeting were able to raise remaining questions and concerns. The SeaGrant team identified the appropriate expertise to address these questions, and these responses were collected and synthesized, producing targeted 8-page publications as well as shorter 1-page essential publications. These shorter 1-page "FAQ" publications included five or six key questions that got to the heart of the primary questions and concerns from the stakeholders. Some were tailored to reach specific communities. For example, there are a number of different fishing communities on the Gulf Cost that are non-English speaking and a number of these publications have been translated into different languages, including Spanish and Vietnamese.

The Sea Grant team not only worked with researchers in the scientific community on the two-way engagement session, but members from the oil spill response community also provided key questions and answers related to dispersant use, emerging technologies and health risks. This was a key finding that arose from a national workshop that was held at the National Academies Gulf research program in Washington DC in 2017, and this finding resulted in a series of five workshops across the US, including Alaska, that identified the various geographic-specific priorities, potential pilot projects, researcher outreach needs and resources that were already in place that might be needed for the future. Multiple sessions during the workshop noted that communication strategies, or rather a lack thereof, related to dispersant use were inadequate and that much of the risk communication efforts really needs to be done PRE-incident and include local communities and expanding education and training. (Figure 12). However, there is acknowledgement that at times, facts and information are not enough to change beliefs. This is evident by prolonged concern of the health impacts of dispersant use, more than 10 years post-incident.

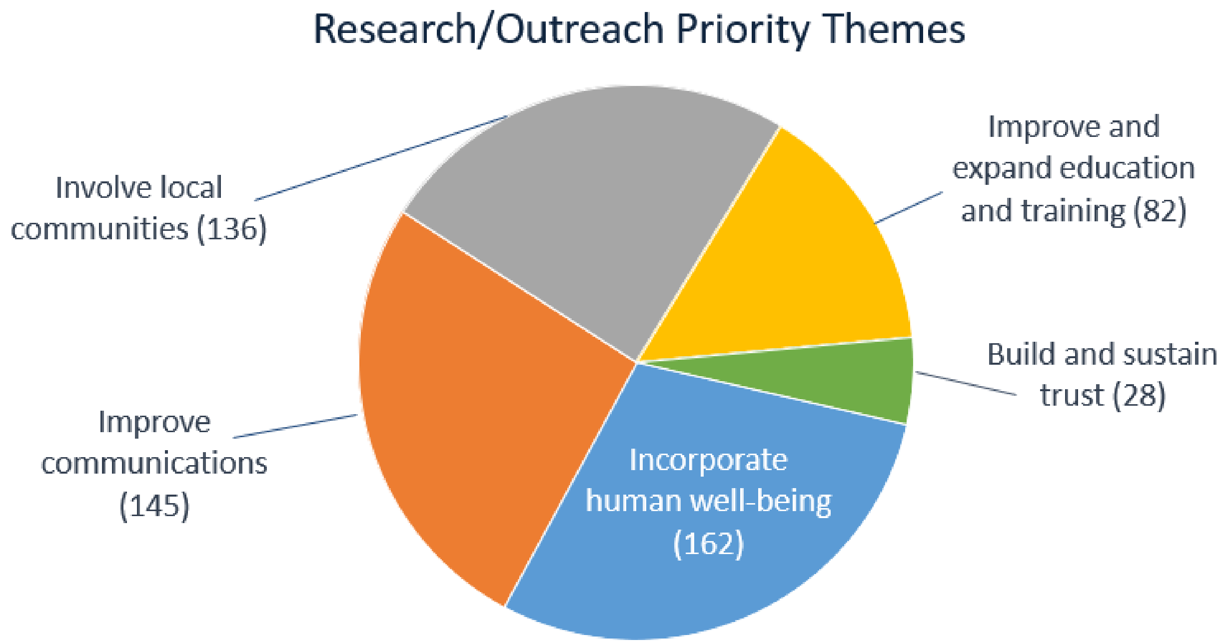

Figure 12. SeaGrant themes during two-way engagement workshops. Note "improve communications" and "incorporate human well-being" were significant priorities.

During these two-way engagement opportunities, the Sea Grant team has learned the best skill at the hand of any communicator is the ability to first listen, and then to frame the responses based on the other person's experience and concern. It is not enough to simply identify the information deficit and then provide that information. Communication teams need to "meet them where they're at". And in the case of the Deepwater Horizon spill, framing communications based on where "they're at" means understanding the multiple stressors encountered by the citizens of the Gulf coast such as back-to-back hurricanes and the additive economic impacts of these storms and the spill. A key message from the discussions related to risk communications is that 11 years later, the oil spill science community is better prepared, educated and skilled than in 2010 for effective communication strategies.

In assessing how best to compassionately listen to concerns, Maslow's hierarchy of needs must be incorporated into the risk communication plan. Answers to the remaining questions on dispersant use were viewed through this lens, fostering better packaging and digestion of information. However, despite these considerations, questions and concerns remain about the use of dispersants related to physical and mental health, socioeconomics, and the environment. Readers are referred to the SeaGrant Oil Spill Outreach site for a full list of their publications: https://gulfseagrant.org/oilspilloutreach/publications/

Q. *To what extent has SeaGrant had workshops for the public relations people at Universities and other academic institutions? At times, the institution's PR staff will want to release statements about research findings. However, at times these can be quite inflammatory and may have unintended consequences beyond just providing the public with information.* **A.** Communications teams have often attended these workshops, but SeaGrant has not held one solely for institutional communicators, though most are careful to keep the information factual. Their job is to do more than just release a catchy headline (or is it)?
Comment: It's the nature of science and scientists to be equivocating and address results with full disclosure on the margins of error. However, when researchers are communicating about health and livelihoods and put margins of error around these issues, the community sees scientists as being "unsure" or indecisive with one another. The scientific community should collectively work on talking about how to address the confidence different scales as the error and work on this language.
Comment: In discussing risk with the public, communication strategies and two-way engagement should focus on real impacts vs perceived impacts, and perhaps enlist guidance from psychologists to help mitigate this.
Comment: Risk communicators should be trained ahead of disasters and should involve local communities prior to disasters as a way to establish trust and lines of communication.
Comment: It is very difficult to overcome beliefs with facts. Beliefs are set early during disasters and it is difficult to change beliefs after they are made.
Comment: Priority needs for engaging community stakeholders is to involve the local communities early, improve communications and establish trust, and incorporate human well-being when responding to community concerns.

Concluding Remarks

The intent of the workshop was to synthesize the findings on dispersants in light of new and emerging GoMRI research and provide some updates to the NASEM dispersant report. It was also to provide a larger context for how and where academic research can contribute to the decision-making process in terms of sampling, prioritizing resources and communicating to the public. Review papers and standardized protocol documents outlining best practices with co-authorship from various agencies and academic institutions would provide consistent messaging and structured guidelines for opportunistic research in the future.

Specifically, the organizing committee sees significant opportunity for progress on the following NASEM recommendations with contributions from the attendees of this workshop.

Recommendation: Decision makers should further evaluate surface and subsea spill scenarios using NEBA tools to better define the range of conditions where dispersant use may be an appropriate option.

Recommendation: Research teams should use standardized toxicity testing methods and analytical chemistry protocols. For testing the effect of dispersant, the variable loading test design should be used. From this, a clearinghouse for experimental protocols should be developed.

Recommendation: Research should use toxic units in revised oil toxicity testing standards, evaluation criteria for models, and response option risk analysis. Using toxicity metrics such as HC5 and LC50 for toxicity models may be more appropriate.

Recommendation: Provide the selection of biomarkers to improve human exposure assessment. Add to list of the U.S. Environmental Protection Agency's (EPA's) National Contingency Plan Product Schedule.

Recommendation: Implement reporting requirements for details of injury and illness reporting for worker health and safety should be improved.

Recommendation: The NEBA tools should be expanded to address the health of response personnel, community health, and socioeconomic considerations.

Recommendation: Efforts to take detailed scientific measurements during future spills (spills of opportunity) and/or to conduct dedicated field experiments should be strongly encouraged. There were also some key recommendations from the workshop participants beyond these:

Recommendation: A peer-reviewed paper should be developed that summarizes the "common ground" landscape that has been discussed at GoMRI conferences and meetings. This could be easily referenced and widely accessible, perhaps in EOS or Marine Pollution Bulletin.

Recommendation: A best practice document should be developed for laboratory-based studies by a working group comprised of academic, governmental, industry, consulting companies, and non-profit organization researchers. This would send a powerful message to the community and have been an extremely valuable document to have in 2011.

Recommendation: There is a need to better define what is meant by the terms 'environmentally relevant', or ' real-world relevant' given the wide range of scales for space, time, and petroleum chemical and the concentrations of their reaction products in the environment after a spill. This should be coupled with recommendations for the range of experimental conditions and concentrations of oil chemicals and oil chemical-dispersant mixtures for exposures in laboratory and mesocosm experiments and the rational for what effects are being assessed, e.g. lethal, sub-lethal, organism interactions. When publishing results from laboratory-based experiments, the real-world relevance or applicability should be addressed in the paper. This would help with advocacy and might be a topic for a "viewpoint" article in Marine Pollution Bulletin. This recommendation ties in many of the previous items.

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Workshop Attendees

Adriana Bejarano, Shell Health-Americas	Emily Maung-Douglass, LA Sea Grant
Michel Boufadel, New Jersey Institute of Technology	Alon McCormick, University of Minnesota
Peter Brewer, MBARI	Joy McGrath, Exponent
Victoria Broje, Shell Projects and Technology	Carys Mitchelmore, UMCES
Ed Buskey, University of Texas	Steven Murawski, University of South Florida
Gina Coelho, Sponson Group, Inc.	Tim Nedwed, ExxonMobil
Robyn Conmy, EPA Office of Research and Development	Paul Nony, CTEH
Tom Coolbaugh, Applied Research Associates, Ohmsett	Claire Paris, University of Miami
Richard Dodge, Nova Southeastern University	Missy Partyka, MS/AL Sea Grant
Paige Doelling, NOAA	Jennifer Petitt, AIBS
John Farrington, WHOI	Roger Prince, formerly Exxon Mobil
Michael Feldman, Consortium for Ocean Leadership	Nathan Putnam, LGL Ecological Research Associates
Joel Fodrie, University of North Carolina-Chapel Hill	Jürgen Rullkötter, University of Oldenburg
Sherryl Gilbert, University of South Florida	Mike Sams, USCG
Jonas Gros, GEOMAR Helmholtz Centre for Ocean Research	Michael Schlüter, TUHH, Hamburg University of Technology
Martin Grosell, University of Miami	Kevin Shaw, GoMRI
Doug Helton, NOAA	Burt Singer, Univeristy of Florida
Vijay John, Tulane University	Helena Solo-Gabriele, University of Miami
Samantha Joye, University of Georgia	Kalliat Valsaraj, LSU
Susan Kane Driscoll, Exponent	Terry Wade, Texas A&M University
Joseph Katz, Johns Hopkins	Chuck Wilson, GoMRI
Nancy Kinner, UNH, CRRC	Callan Yanoff, Consortium for Ocean Leadership
Ronald Larson, University of Michigan	Kai Ziervogel, UNH
Ken Lee, DFO, Canada	Leigh Zimmermann, Consortium for Ocean Leadership