

Dispersants Forum:
**Gulf of Mexico Oil Spill & Ecosystem Science
Conference**

What have we learned, and what are the opportunities
for improvement to better inform decision making?

Sunday, January 26, 2014

Mobile, Alabama

Facilitated by:

**Center for Spills in the Environment
University of New Hampshire**



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ACKNOWLEDGEMENTS

The content for this workshop was developed in cooperation with the Gulf of Mexico Research Initiative (GoMRI) Research Board: Dr. Charles Wilson, Chief Scientist for GoMRI; Dr. Peter Brewer, Senior Scientist Monterey Bay Aquarium Research Institute; Dr. John Farrington, Dean Emeritus, Woods Hole Oceanographic Institution; and Dr. Michael Carron, Program Director for GoMRI. Since the 2010 DWH oil spill, GoMRI researchers have investigated the impacts of the oil, dispersed oil, and dispersant on the ecosystems of the Gulf of Mexico and affected coastal states in a broad context of improving fundamental understanding of the dynamics of oil spills and their environmental stresses and public health implications. The ultimate goal of GoMRI will be 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. Knowledge accrued will be applied to restoration and improving the long-term environmental health of the Gulf of Mexico.

This workshop was facilitated by Dr. Nancy Kinner, Center for Spills in the Environment (CSE) at the University of New Hampshire (UNH). CSE focuses on issues related to hydrocarbon spills. The Center is known for its independence and excellence in the areas of environmental engineering and marine science as they relate to spills. CSE has conducted numerous workshops bringing together researchers, practitioners, as well as scientists of diverse backgrounds (including from industry and NGOs) to address issues in spill response, restoration and recovery.

We wish to thank all speakers for their participation in the Forum's panels. This effort would not have been possible without their collective efforts.

Dr. Charles Wilson, Chief Scientist for GoMRI

Dr. Nancy E. Kinner, Center for Spills in the Environment, University of New Hampshire

Dr. Charles Henry, NOAA, Office of Response & Restoration, Gulf of Mexico Disaster Response Center

Dr. Ronald Tjeerdema, University of California, Davis, Department of Environmental Toxicology

Michael Sams, U.S. Coast Guard, District 8

Dr. Thomas Coolbaugh, ExxonMobil, Research & Engineering, Oil Spill Response Technology

Dr. Richard Knudsen, State of Florida, Fish & Wildlife Conservation commission, Scientific Support Coordinator for Oil Spills

Dr. Vijay John, Tulane University, GoMRI Consortium for the Molecular Engineering of Dispersant Systems (CMEDS)

Dr. Robert Dickey, University of Texas, Marine Science Institute

Dr. Christopher Robbins, Ocean Conservancy

Dr. Edward Buskey, University of Texas, GoMRI, Dispersion Research on Oil: Physics and Plankton Studies Consortium (DROPPS)

Dr. James Fabisiak, University of Pittsburgh, Department of Environmental & Occupational Health

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1. INTRODUCTION

The GoMRI Research Board, as part of the 2014 Gulf of Mexico Oil Spill & Ecosystem Science Conference, convened a Forum to discuss the current understanding of dispersants and their use and application following the Deepwater Horizon (DWH) spill in 2010. The Forum was organized into a Plenary Session that provided an overview of dispersant response strategies and effects. This was followed by panels on: 1) Response, and 2) Effects. The panelists included practitioners, scientists, an industry representative and other stakeholders to provide a broad perspective on dispersant issues. Panelists presented personal or agency perspectives on: what was known about dispersants before DWH; what we learned from DWH that will inform future dispersant application; what data gaps and concerns exist; and what future needs exist for developing and applying dispersants effectively. They also considered new frontiers from related fields that could improve dispersants and its application. The GoMRI Research Board envisioned that this workshop could be the basis for future gatherings on: (1) the research needed on dispersants and, (2) the information needed to inform policy and management decisions about when and how to use dispersants during spills.

2. PLENARY SESSION

2.1. Introduction – Dr. Charles Wilson, GoMRI

Charles Wilson opened the workshop by introducing the objectives that the GoMRI Research Board hoped to achieve by sponsoring the workshop. GoMRI recognized that there have been a number of meetings and reports that have discussed the use of dispersants and in particular the use of dispersants during DWH. The Research Board felt strongly that in order to be able to take the next steps regarding the use of dispersants, it was important to establish a dialog among researchers, practitioners, NGOs and the public about lessons learned and future uses of dispersants during spills. Researchers and developers of new dispersants also need to understand the decision processes used by practitioners during a spill regarding dispersants.

2.2. Dispersants and Their Use in Spill Response – Dr. Charles Henry, NOAA, Office of Response & Restoration, Gulf of Mexico Disaster Response Center

Charles Henry stressed that during a spill there is little time to evaluate various options to contain a spill and limit its environmental impacts. Thus, it is important for response professionals to understand the strengths and limitations of all the “tools” in the toolbox,

including dispersants so that given response actions can effectively control the spill with as little harm to the environment as possible. The fundamentals of any response strategy are:

- Protection of human life
- Source control
- Containment of the oil at or near the source
- Protection of sensitive habitats/environments
- Recovery of spilled oil
- Mitigation to minimize environmental impacts from the spill and enhance natural recovery and restoration

During the DWH spill, response decisions were impacted by the size of the spill and the fact that the source was approximately 1600 meters below the water surface. Dispersants have the advantage of being applied by aerial application which can treat large amounts of oil on the water's surface over a large area rapidly. Responders use dispersants to reduce the impacts to beaches and sensitive shoreline (e.g., marshes) and to sensitive species such as marine mammals and birds.

During the DWH, the subsurface application of dispersant was used to reduce the amount of oil reaching the surface. This was the first time subsurface injection of dispersants had ever been tried. The decision to inject dispersants into the subsurface followed an adaptive management strategy:

- Developing proper mixing and residence times;
- Evaluating dispersed plume transport (where would it go?);
- Evaluating receptors or natural resources at risk;
- Monitoring for efficacy and effectiveness; and
- Evaluating spill/response tradeoffs.

Dispersant use, like any response strategy, is a trade-off. It has the potential to increase risk to organisms in the water column, while reducing injury to surface water and shoreline species. Response practitioners need all the information available about any response strategy, including dispersants, prior to a spill to make the best decisions. An on-going dialog with dispersant scientists and response practitioners will greatly improve that decision-making process during a spill.

2.3. Characterizing Dispersant and Dispersed Oil Effects- Dr. Ronald Tjeerdema, University of California, Davis, Department of Environmental Toxicology

Dispersants enhance weathering and degradation of the oil plume. They also facilitate oil being biodegraded by bacteria. Responders, in deciding whether to apply dispersants to a spill, need to consider resource impacts from the oil itself vs. potential impacts of the dispersants and dispersed oil.

Corexit 9527 toxicity studies, performed with constant and spiked concentrations showed that constant concentrations were more toxic in the aqueous plume than spiked (transient) concentrations (concentrations range = 20 – 150 ppm). Spiked concentrations probably are a better representation of real conditions, however. Toxicity of dispersants is species, life-stage, feeding type and endpoint specific. Even the specific formulation is important; for example, toxicity studies comparing Corexit 9500 and 9527 showed that the two dispersants had similar results for abalone, but not for mysids.

The experimental design used to gather the data is very important. Water accommodated fractions (WAF) and chemically enhanced (dispersant) water accommodated fractions (CEWAF) can have different results for toxicity depending on species, life stage, exposure, endpoint and chemical analysis. For example, Corexit 9500 decreased oil lethality to fishes some 7 to 20-fold – based on a total hydrocarbon lethal concentration (LC₅₀). In the environment, toxicity occurs primarily from the dissolved fraction of the oil where the WAF and CEWAF give similar results. Metabolic impacts are possibly due to bioavailable fractions. Thus, caution must be used in comparing literature values for toxicity. Future studies need to provide standardized results and methodologies for dispersant and dispersant/oil testing.

3. RESPONSE PANEL

The Response Panel was populated by practitioners and scientists familiar with the use of dispersants during DWH.

3.1. Michael Sams: U.S. Coast Guard, District 8

The Federal On-Scene Coordinator (FOSC) for an oil spill response needs to have all options available in the “tool box”, including dispersants. The U.S. Coast Guard always wants to fight oil spills offshore, away from beaches and critical wetland and shoreline habitats, if at all possible.

[N.B., For marine spills, the U.S. Coast Guard's member of the Unified Command is the FOSC.]
The Coast Guard believes that the use of dispersants was effective during DWH.

During DWH, approximately 1.8 million gallons were applied (surface 1,000,000 gal and subsurface 770,000 gal). The Coast Guard, as part of the Incidence Response Preparedness Review (ISPR), requested that the National Response Team (NRT) perform an intensive analysis of all aspects of dispersant use during the DWH incident. This analysis can be the catalyst for development of national standards and guidelines for Regional Response Teams (RRT).

The Coast Guard continues to monitor development of new dispersant products as well as improvements in methods of dispersant application. Specifically, there is interest in refining the aerial application of dispersants and exploring the use of subsea dispersants on deep well incidents. Companies are developing capping stacks that could be applied within 10 days to stop the flow from wells. This will be an important tool to add to the "tool box".

3.2. Dr. Thomas Coolbaugh: ExxonMobil Research & Engineering, Oil Spill Response Technology

Dispersants are solutions of surfactants that reduce oil-water interfacial tension allowing slicks to break into very small droplets enhancing the natural biodegradation process. In typical conditions, where oxygen and nutrients are generally not limiting in the water column, dispersants speed the biodegradation of oil in surface waters as the oil becomes more bioavailable.

During the DWH spill, there was a 4 hour rise rate for oil to travel from the well head to the surface. The initial test of subsea dispersant injected on May 9 – 10, 2010, showed substantial evidence of as much as 90% less oil reaching the surface. Industry believes that dispersant use may present significant advantages over mechanical recovery and should be considered as a primary response tool in future incident operations. In particular, subsea injection is seen as a step-change advance that may reduce spill impacts by an order of magnitude, and decrease the volume of dispersant required. Industry continues to work on optimizing subsea injection, new methods of application, and new dispersant products.

3.3. Dr. Richard Knudsen: Florida Fish & Wildlife Conservation Commission, Scientific Support Coordinator for Oil Spills

Richard Knudsen provided a state perspective on the use of dispersants during DWH. State authority over resources ends three miles offshore. The state agencies are concerned with a variety of natural resources (e.g., beaches, critical, fish, and wildlife). From a state responder perspective, dispersants reduce shoreline impacts from a spill and subsea dispersant use is a valuable tool in the responder's "toolbox", if it can be justified. Dispersant applications will typically be evaluated on a case-by-case basis by state or federal government agencies. It is important to understand that dispersant use is considered a very complex and politically contentious issue at all levels of government, as well as by the public.

Going forward questions still remain about the impacts - short and long term - from the use of large amounts of dispersants during DWH. The use of science and technology has the potential to make the decision-making process for response professionals more effective. As an example, nanotechnology may hold promise as a potential alternative to chemical dispersants. Science-driven spatial technology, such as advanced GIS applications, will also be an important tool in future decision-making by response professionals.

3.4. Dr. Vijay John: Tulane University, GoMRI Consortium for the Molecular Engineering of Dispersant Systems (CMEDS)

Vijay John leads the CMEDS GoMRI Consortium which is conducting research to develop new dispersant technology that can be applied to spill response. Specifically, CMEDS is studying the dynamics of the oil-water interface when dispersants are applied. CMEDS is working to determine if there are new classes of environmentally-benign dispersants that could be developed based on biopolymers, biosurfactants, and interfacially-stabilized particles. The consortium team is also studying whether the physics of naturally occurring phenomena (e.g., oil-mineral aggregates) can aid in the design of dispersants. New systems and methods of delivery are being designed that minimize use of solvents and can be tuned to varying environmental conditions.

The CMEDs research is examining a number of new classes of dispersants and applications that might enhance the response “tool box” with potentially reduced environmental impacts. These include:

- High efficiency dispersants that work at low concentrations,
- Green and natural dispersants (low toxicity, biodegradable, nutrient loaded),
- Dispersants that adhere and mix with oils,
- Herders and gelators to recover or burn oil,
- Imaging agents for dispersed oil (magnetic), and
- Capsules/microgels for controlled release of dispersants.

3.5. Dr. Charles Henry, NOAA, ORR, Gulf of Mexico Disaster Response Center

The use of dispersants is one of a number of options that the response team has to address in a spill. As part of the decision process, the team needs to consider the type and size of the spill, the resources that potentially could be impacted, and containment at the source. Aerial application of dispersants can mitigate large amounts of oil, if treated promptly. It can mitigate the overall impact of an oil spill to the environment and particularly coastal resources. Clearly, dispersant use is a trade-off with the potential for increased risk to the natural resources in the water column and formation of Marine Oil Snow Sedimentation and Flocculent Accumulation (MOSSFA) that may impact the benthos.

The culture of response professionals is to “do no more harm than good”. The challenge for response professionals is to have as much knowledge as possible about the various response tools, the strengths and impacts of each. With respect to dispersants, DWH was the first opportunity to gain knowledge that can be applied to future spills. There is a lot to be learned from field conditions in determining the behavior of dispersants. Information regarding dispersant use in the DWH response continues to be evaluated. It will be extremely important for researchers and response professionals to share information, so that future response actions that involve dispersants will have fewer environmental impacts and be more effective.

4. EFFECTS PANEL

The Effects Panel consisted of researchers who were involved in the assessment of impacts from the DWH spill.

4.1 Dr. Robert Dickey: University of Texas, Marine Science Institute

Many of the compounds in the Corexit dispersants are commonly found in other products such as cosmetics, drugs and personal care products. Corexit does not have a high capacity to be taken up by cells. The results of studies following DWH have shown that seafood safety in the Gulf was not a problem as long as the oil concentration in the water decreased. There is a need, however, to have a complete search of the literature to understand the toxicity for various components of dispersants. As in any toxicity research, it is important to have a standardization of methods, so studies are comparable.

4.2 Dr. Christopher Robbins: Ocean Conservancy, Restoration Planning

Christopher Robbins provided insight from the NGO perspective. He questioned whether we really know all of the trade-offs related to the use of dispersants during the DWH spill response. We do not have the final empirical data on the efficacy of the dispersants applied, the best methodologies for the application nor the most effective concentrations. Questions still remain as to the toxicity of oil alone versus that of the oil and dispersant together. Additional toxicity studies are needed, along with continued long term monitoring of the Gulf, to answer questions related to biotic and food web impacts of the dispersant use.

It is important to address issues related to dispersant use to reduce public skepticism. With oil and gas development continuing to occur at greater water depths, it is important to develop effective monitoring programs and reduce critical research gaps. It is also important to improve data transparency and improve public outreach on this important subject.

4.3 Dr. Thomas Coolbaugh: ExxonMobil Research & Engineering, Oil Spill Response Technology

In order to understand the impacts of dispersants, we need to understand the ambient conditions and the actual concentrations of constituents during the spill. During a spill, *in situ* concentrations are low due to the rapid dilution of oil. Rapid dilution limits ecosystem impacts of both dispersant and dispersed oil (i.e., concentrations start low and decrease quickly). Toxicity studies are difficult to conduct at these concentrations and thus it is difficult to interpret them for real world conditions. Many studies involve high constant concentrations of dispersant or dispersed oil and long exposures. Lab toxicity tests should reflect real world exposures (e.g., protocols developed by Chemical Response to Oil Spills: Ecological Research Forum (CROSERF)).

It is important to consider potential tradeoffs during the spill response decision-making process. The goal of the response should be to minimize negative consequences of the spill, balancing all impacts. Each spill is different and all response options should be considered in the Net Environmental Benefit Analysis (NEBA).

4.4 Dr. Edward Buskey: University of Texas, GoMRI, Dispersion Research on Oil: Physics and Plankton Studies Consortium (DROPPS)

Studies of physical processes have shown how surface oil breaks up and disperses in the ocean. Processes such as surface waves and rain drops impacting the spill surface produce micron-sized droplets in air and water. Biological activity, such as feeding currents and swimming behavior of plankton, can also contribute to the rate at which chemically-treated oil is dispersed. The aerosols produced when spraying dispersants on the surface oil may be a health hazard to humans and wildlife, if they occur in high enough concentrations.

Zooplankton, protozoa and copepods ingest oil droplets that are in the size range of their normal food particles. Ingested toxic PAHs are readily absorbed and concentrated in crustacean zooplankton. The volume of oil at which toxic thresholds are exceeded is small, and since zooplankton reproduce rapidly; hence, there is a relatively small impact of ingested oil on these biota.

Smaller subsurface oil droplets that pass through the water column rise slowly and degrade faster. Their greater surface to volume ratio permits a greater opportunity for dissolution of

soluble oil compounds from the droplet. More surface area also permits a greater amount of colonization of the oil droplets by oil degrading bacteria. Bacterial films also have the ability to modify the surficial properties of oil droplets.

The results of the DROPPS Consortium's studies indicate the importance of small oil droplets to the biodegradation of oil. The ability of dispersants to create very small oil droplets further contributes to these observed effects.

4.5 Dr. James Fabisiak: University of Pittsburgh, Dept. of Environmental & Occupational Health

There are four steps to a risk assessment: hazard identification, dose response, exposure assessment, and risk assessment. A hazard identification for dispersants shows that the components of Corexit are not highly toxic. For other dispersants, there are a number of constituents that are considered proprietary, so the toxicity is not completely known. The dose response analysis for Corexit indicates that high concentrations, not observed in dispersant applications, are required to elicit any human response.

It is difficult to assess risk because of the lack of control of dispersant concentrations in the environment. Occupational exposure to cleanup workers was probably greater than exposure to individuals in the public. Assuming $\approx 10\%$ of Gulf was affected by DWH spill, and that water was mixed with the total volume of dispersant used (1.8 million gal); an individual would need to drink about 3 million gallons of the water to get the amount of DOSS contained in one dose of stool softener. There are several on-going studies trying to assess the impacts of dispersants on humans. The results of these studies are difficult to assess because of the problems determining actual exposure.

5. Conclusions from the Forum

The presentations and the subsequent discussion that followed at the Forum, resulted in a number of conclusions and unanswered questions which should be part of the continued dialogue regarding the use of dispersants and their impacts.

Conclusions:

- The goal of all incident response is to “do no more harm than good” using tools that are available, including dispersants.
- An index is needed of the various studies from the peer-reviewed and grey literature on dispersants, including their efficacy, toxicity and impacts.
- Improved communication between response practitioners and researchers is needed so each group has a better understanding of the data required to provide better incident response, particularly with respect to dispersants.
- Response professionals need as much information as possible on dispersants efficacy and impacts prior to a spill so that better decisions can be made efficiently and effectively during an incident.
- Toxicity studies on topics, including on the chronic effects of oil, dispersed oil and dispersants, need to be conducted using concentrations observed in the field.
- Information about dispersants needs to be transparent and made available to the public in understandable language.
- Dispersants use offshore minimizes oil coming ashore in mangroves and marshes thereby avoiding accompanying potential adverse impacts in mangroves and marshes for immediate and longer term time scales based on previous oil spill studies.
- Consideration must be given to habitats and rates of recovery as part of the response decision-making process. Mechanical cleanup methods may result in more destruction to habitats, so all response options need to be taken into consideration. Strong vibrant populations of a species might be able to withstand the impact of dispersants, but an endangered species might not.
- Ecological mapping and advanced GIS are effective tools for determining incident response.

Topics Requiring Further Research:

- What is the status of mass balance studies of dispersants used in the DWH spill? What is the fate of the constituents of the dispersed oil and dispersants? MOSSFA needs to be part of these investigations.
- What is the status of new dispersants? How effective are they in dispersing oil? What are their impacts? Can they be distributed effectively?

- There needs to be more data on the effectiveness of dispersants depending on oil type, salinity and environmental conditions.
- Research is needed to investigate subsea dispersant application to answer the following questions: what are the most effective dispersants for subsea use; when should they be used; what are the most effective application methods and rates; and how can we predict/measure effectiveness?
- Resources at risk to dispersed oil needed to be identified using population sensitivity and ecosystem consequence analyses that consider: key populations at risk considering lethal and chronic impacts; recovery rates; and food web consequences. Population sensitivity assessment can inform many decisions (e.g., ecological to economic), as well as identify data gaps, and identify key species that drive tradeoff decisions.

Appendix

Agenda Presentations

[Note: all presentations are also publicly available on CSE website>>
http://crrc.unh.edu/gomri_dispersant_forum]



Dispersants Session: GoMRI Conference
Sunday, January 26, 2014 (1 – 5 pm)
Grand Bay Ballroom

Dispersants: what do we know and what do we need to learn, to better inform decisions about their use?

Topics:

- Response, Effects and Damage Assessment (associated with dispersants and dispersed oil);
- Recovery and Restoration (how are recovery and restoration is different if dispersants are used during a response); and
- Lessons Learned from DWH about Dispersants Use; Questions that remain; New frontiers with respect to dispersant use.

Facilitated by: Dr. Nancy E. Kinner University of New Hampshire, Center for Spills in the Environment.

- 1:00 pm Plenary: Dispersants & Their Use in Spill Response *Charlie Henry, NOAA*
Plenary - Effects & Damage Assessment and Recovery & Restoration *Ron Tjeerdema, UC Davis*
- 2:00 pm Response Panel:
Michael Sams, USCG
Charlie Henry, NOAA
Tom Coolbaugh, ExxonMobil
Richard Knudsen, State of Florida
Vijay John, CMEDS, Tulane
- 2:30 pm Effects/Impacts Panel
Robert Dickey, Univ of Texas
Chris Robbins, Ocean Conservancy
Tom Coolbaugh, ExxonMobil
Ed Buskey, DROPPS, Univ of Texas
James Fabisiak, Univ of Pittsburgh
- 3:00 pm Break
3:30 pm Audience Q & A
5:00 pm Adjourn

Dispersants: What Do We Know and What Do We Need to Learn to Better Inform Decisions About Their Use?

GoMRI Conference
Mobile, Alabama
January 26, 2014



Center for Spills in the Environment

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Dispersants: What Do We Know and What Do We Need to Learn to Better Inform Decisions About Their Use?

Nancy E. Kinner
Center for Spills in the Environment
University of New Hampshire
January 26, 2014



Center for Spills in the Environment

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Logistics

- Fire exits
- Restrooms
- Questions about logistics see Kathy Mandsager or me



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GoMRI Dispersants Forum

- Hosted by GoMRI Research Board
- Facilitated by Center for Spills in the Environment



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**Coastal Response
Research Center**
(NOAA \$)

**Center for Spills in
the Environment**
(Non-NOAA \$)

- Conduct and Oversee Basic and Applied Research and Outreach on Spill Response and Restoration
- Transform Research Results into Practice
- Serve as Hub for Oil Spill R&D (ALL Stakeholders)
- Facilitate Collaboration on R&D Among Stakeholders



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**Center for Spills in the
Environment**
(GoMRI Research Board \$)

- Conduct and Oversee Basic and Applied Research and Outreach on Spill Response and Restoration
- Transform Research Results into Practice
- Serve as Hub for Oil Spill R&D (ALL Stakeholders)
- Facilitate Collaboration on R&D Among Stakeholders



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Purpose of Forum

- Discuss understanding of dispersants and their use and application
- Specific Questions:
 - What do we know about dispersants
 - Lessons learned from DWH
 - Questions remaining
 - New frontiers



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Desired Outcomes of Forum

- Open conversation to share perspectives
- Basis for future gatherings on dispersants research
 - Informing policy and management decisions about when and how to use dispersants during spills
- CSE will produce summary report



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Format of Today's Forum

- Plenary Talks:
 - Response: Dispersants and Their Use in Spills
 - Effects/Damage Assessment of Dispersants and Dispersed Oil
- Panels: Response and Effects
 - Lessons learned, Questions Remaining, New Frontiers
- Dialogue with Audience



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Agenda

- Opening Remarks:
 - **Chuck Wilson**: Chief Scientist GoMRI
- Plenary Talks:
 - **Charlie Henry**: NOAA Office of Response and Restoration
 - **Ron Tjeerdema**: UC Davis Dept. Environmental Toxicology



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Agenda

- Panels:
 - Response:
 - Michael Sams: US Coast Guard
 - Tom Coolbaugh: ExxonMobil
 - Richard Knudsen: State of Florida
 - Vijay John: GoMRI CMEDS, Tulane University
 - Effects...
 - Robert Dickey: Univ. Texas
 - Chris Robbins: Ocean Conservancy
 - Tom Coolbaugh: ExxonMobil
 - Jim Fabisiak: Univ. Pittsburgh
 - Edward Buskey: GoMRI DROPPS, Univ. Texas



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Agenda

- Discussion/Dialog:
 - Protocol:
 - Use microphone
 - State:
 - Name
 - Affiliation



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Facilitation Pledge

- I will recognize and encourage everyone to speak
- I commit to:
 - Being neutral, fair, kind, and faithful to the process
- Stop me if I am not doing this!



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Discussion

- Listen to and hear one another
- Respect each other's views
- Open discussion and dialog
- Range of views will be documented and reflected in summary report
- Provide benefit/perspectives to all
- Basis for future gatherings on dispersants research



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Agenda

- Opening Remarks:
 - **Chuck Wilson**: Chief Scientist GoMRI
- Plenary Talks:
 - **Charlie Henry**: NOAA Office of Response and Restoration
 - **Ron Tjeerdema**: UC Davis Dept. Environmental Toxicology



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- CSE will produce summary report



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**Dispersants: What have we learned,
and opportunities for improvement to better
inform decision making relevant to dispersants
and their use?**

GOMRI Conference, Mobile, Alabama

SETTING THE STAGE

Charlie Henry

(former NOAA Scientific Support Coordinator)

Disclaimer:

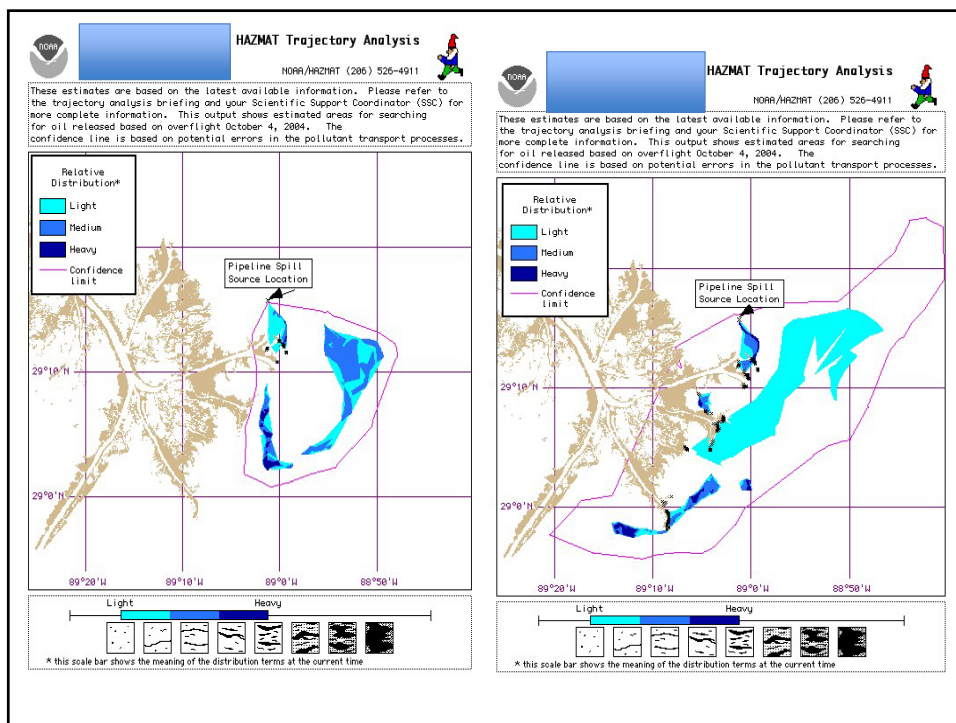
The information presented reflects only the views of the presenter,
and does not necessarily reflect the official positions or policies of
NOAA or the Department of Commerce.

**THIS IS THE TIME TO DISCUSS
PROS AND CONS
POSITIVES AND NEGATIVES
ALTERNATIVES**

THERE IS LITTLE TIME DURING AN EVENT

**THIS IS JUST AN EXERCISE
THIS IS A DRILL
THIS IS A REAL POSSIBILITY**

- Last night - Pipeline Failure off the Mississippi River Delta
- Source control – Ends of Pipeline Shut – Pot. 40K BBL
- Equipment has be mobilized
- The GRP is being used to identify and protect sensitive coastal areas (takes time – cannot deploy at night)
- Before mid-morning today – overflights have mapped a large slick off the Louisiana Coast





**THIS IS JUST AN EXERCISE
THIS IS A DRILL
THIS IS A REAL POSSIBILITY**

- Last night - Pipeline Failure off the Mississippi River Delta
- Source control – Ends of Pipeline Shut – Pot. 40K BBL
- Equipment has be mobilized
- The GRP is being used to identify and protect sensitive coastal areas (takes time – cannot deploy at night)
- Before mid-morning today – overflights have mapped a large slick off the Louisiana Coast
- **At 1:00 PM today – RP has requested the tactical use of aerial dispersants to FOSC. Sunset is 5:32 PM (before 3:30 PM a final decision is required)**

Setting a Foundation

- **Response Culture - Do No More Harm Than Good**
- **Response Strategy and Deepwater Horizon Challenges**
- **What are Dispersants? Why are dispersants considered in strategic and tactical response planning?**

Fundamental Oil Spill Response Strategy

- **Prevention**
- **Protection of Life**
- **Source control**
- **Contain the oil at or near the source**
- **Protect sensitive habitats/environments**
- **Recover spilled oil**
- **Mitigation - Minimize environmental impact from the spill and enhance natural recovery**

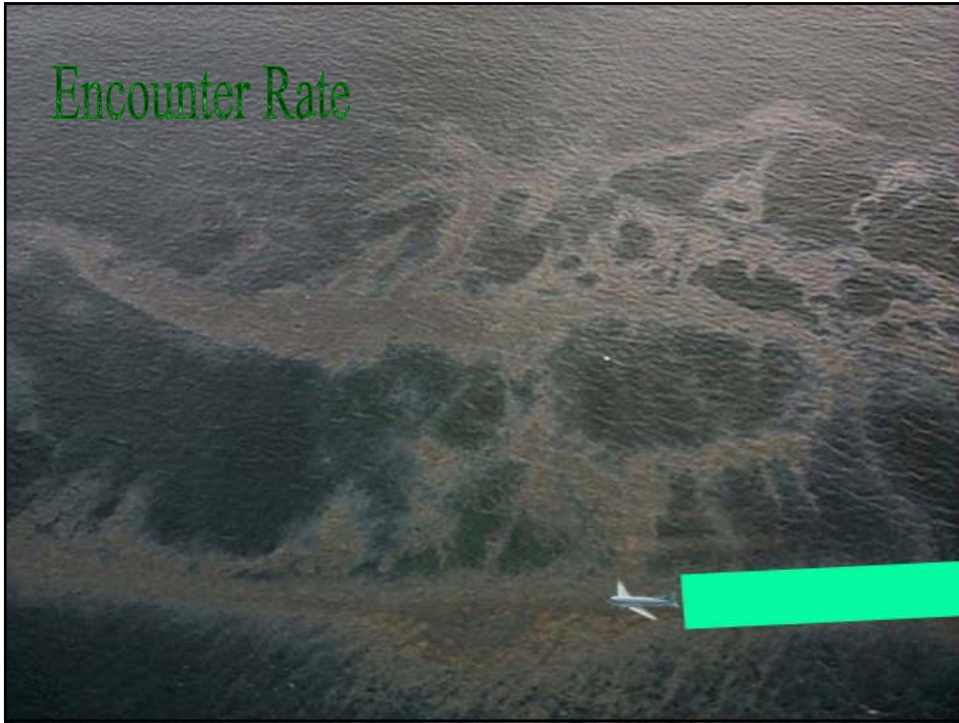


Deepwater Horizon Incident - Challenges

- **Prevention**
- **Protection of Life (11 fatalities)**
- **Source control**
- **Contain the oil at or near the source**

- **Protect sensitive habitats/environments**
- **Recover spilled oil**

- **Mitigation - Minimize environmental impact from the spill and enhance natural recovery**



What are Dispersants?

What do they do?

(Surface Application)

G “Mixtures of solvents and surfactants”

LIPOPHOBIC
HYDROPHILIC
(WATER LOVING)



HYDROPHOBIC
LIPOPHILIC
(OIL LOVING)

15

“...just Like Dawn™ Detergent (?)”

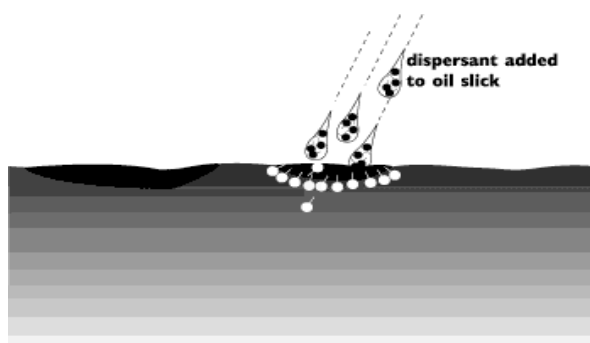
- u Dispersants, like detergents, reduce the interfacial tension between water and oil, permitting the oil to break into tiny droplets. The function of the solvent is to reduce the viscosity of the surfactants. The solvent may also aid in surfactant-oil interaction.
- u “For good or bad” - Dispersants enhance a natural process.”

16

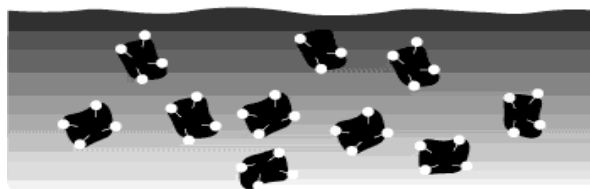
- Dispersed oil is not “gone” from the environment.
- The ultimate fate of oil spilled in the marine environment is biodegradation.
- Dispersion enhances the rate of natural biodegradation by increasing the surface area of the spilled oil – it also changes where oil is in the environment (trade-offs).

17

How Do Dispersants Work?



One end of each dispersant molecule 'chain' attaches to water molecules while the other end of the 'chain' attaches to the oil droplets.

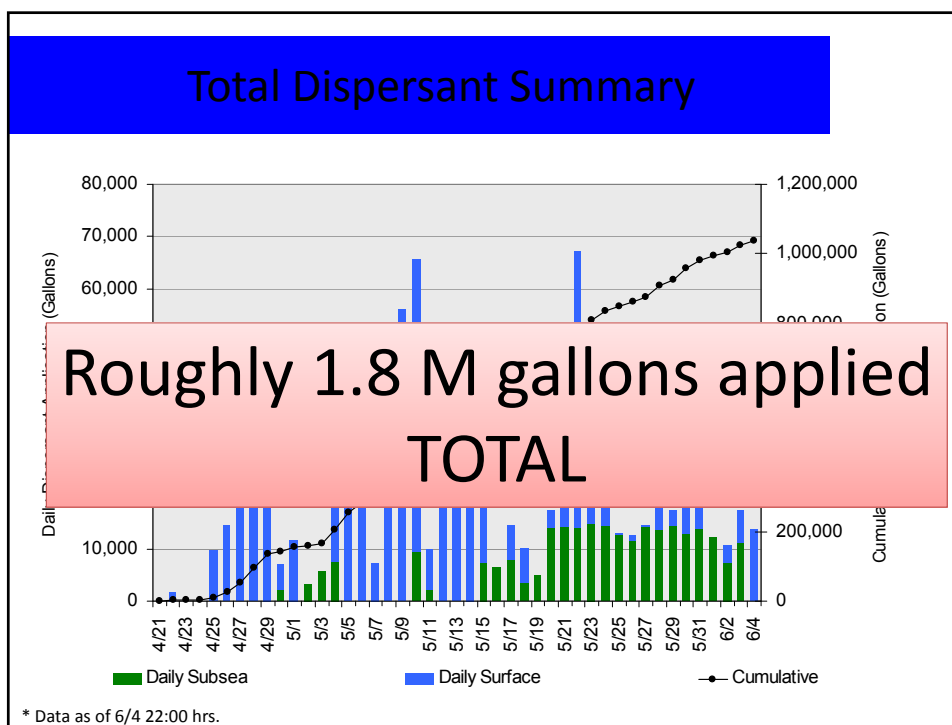


A little energy from wind and waves breaks the oil slick into smaller oil droplets surrounded by dispersant molecules as shown.

Again, why consider using dispersants?

- ✓ Aerial application of dispersants can mitigate large amounts of oil if treated promptly.
- ✓ Mitigate -- reduce the overall impact of an oil spill to the environment as a whole.
- ✓ Clearly, dispersant use is a **trade-off**: increased risk to the water column to reduce injury to surface water and shoreline resources.

19



Sub-Surface Application

- Operational Issues and Authorization
- Would it even work? (mixing and resonance times)
- Dispersed Plume Transport (Where would it go?)
- Receptors or Natural Resources at Risk (Who would get hit?)
- Overall Spill Trade-offs
- Monitoring for Effectiveness (Efficacy) and Effects
- Adaptive Management Strategy



Setting a Foundation

- Response Culture - Do No More Harm Than Good
- Response Strategy – Deepwater Horizon Challenges
- What are Dispersants?
- Response Culture – “Nothing to be gained by a second kick of a mule.” Learn from Past...
- Spills are unplanned and uncontrolled events.
- “Spills are not true scientific experiments – but there is only so much that can be done in a laboratory.”

Characterizing Dispersant/Dispersed Oil Effects

Ronald S. Tjeerdema
Department of Environmental Toxicology
University of California, Davis

Characterizing Dispersant/Dispersed Oil Effects

Ronald S. Tjeerdema
Department of Environmental Toxicology
University of California, Davis

Topics

- The Responder's Toolbox
- Bioassays – WAF vs CEWAF
- Metabolomics – WAF vs CEWAF
- Chemistry and Bioavailability
- Conclusions

- The Responder's Toolbox
- Bioassays – WAF vs CEWAF
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- Conclusions



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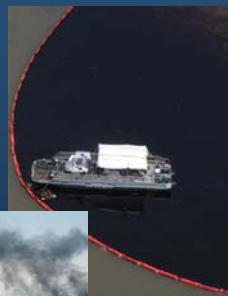


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I. The Responder's Toolbox

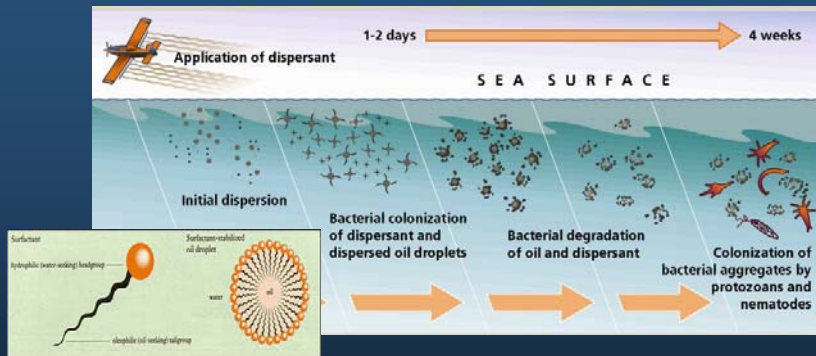


- Collection
- Burning
- Bioremediation
- *Dispersants*



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Dispersants Enhance Weathering



- Dispersants are similar to domestic detergents
- They break up oil and remove it from the surface
- Droplets may be more readily digested by bacteria

Resources and Impacts

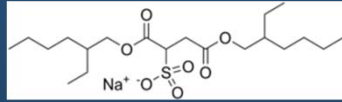
- Dispersants may reduce slicks and shoreline impacts
- Tool selection may depend on resources at risk and in most in need of protection



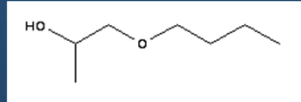
or



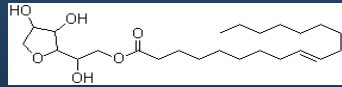
What Makes a Dispersant? Corexit 9500



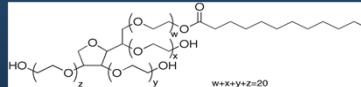
Dioctyl Sodium Sulfosuccinate



Propylene Glycol Butyl Ether



Sorbitan Monooleate



Ethoxylated Sorbitan Monooleate

Petroleum Distillates?

- In water and soils, DOSS degrades by 90% within 12-17 days
- DWH – present at depth in ppb range months after the event

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II. Bioassays – WAF vs CEWAF

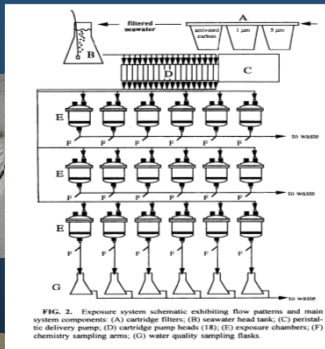


FIG. 2. Exposure system schematic exhibiting flow patterns and main system components. (A) cartridge filters; (B) reservoir head tank; (C) peristaltic delivery pump; (D) cartridge pump heads (18); (E) exposure chambers; (F) chemistry sampling arms; (G) water quality sampling flasks.



Photograph by James Swaidler



Singer et al., *Ecotoxicol. Environ. Saf.* 35:183 (1996)

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Corexit 9527 – Constant versus Spiked

Table 1. Results of flow-through toxicity tests using Corexit 9527^a on early life stages of four marine species

Species	Test	NOEC (ppm)	LC50 (ppm)	95% C.I. LC50	Slope	95% C.I. slope
<i>Haliotis</i>	1	1.19	1.96 ^a	1.89-2.02	7.38	6.35-8.40
	2	1.50	2.20 ^a	2.04-2.36	2.63	2.32-2.94
	3	0.63	1.60 ^a	1.30-1.69	3.98	3.52-4.43
<i>Holmesimysis</i>	1	4.20	7.06	5.97-8.77	4.34	1.99-6.69
	2	4.14	7.26	6.13-8.93	5.51	2.47-8.54
	3	1.66	4.26	3.28-5.37	3.62	1.21-6.02
<i>Atherinops</i>	1	12.3	25.5	19.8-47.7	4.78	-0.52-10.1
	2	14.2	27.9	22.5-34.8	6.14	2.09-10.2
	3	13.9	40.6	32.3-51.0	5.53	2.20-8.86
<i>Macrocyctis</i>	1	<2.35	NC	NC	NC	NC
	2	1.32	NC	NC	NC	NC
	3	2.07	NC	NC	NC	NC

LC50 and slope values derived from probit analysis

NC = not calculated; data inappropriate for calculation.

^aSublethal EC50 values.

^bSignifies that lowest test concentration was significantly different from control.

Singer *et al.*, *Environ. Toxicol. Chem.* 9:1387 (1990)

- Dispersants alone under spiked conditions generally toxic in the range of 20-150 ppm
- Spiked-exposure usually less toxic

Table 2. Results of spiked-exposure toxicity tests using Corexit 9527 on early life stages of four marine species

Species	Test	NOEC (ppm)	MEC (ppm)	95% C.I. MEC
<i>Haliotis</i>	1	5.3	13.6	12.9-14.3
	2	8.4	18.1	16.8-19.5
	3	6.4	15.9	15.1-16.4
<i>Holmesimysis</i>	1	14.9	163.4	140.8-189.5
	2	20.5	136.4	109.5-169.8
	3	8.4	120.4	89.3-162.5
<i>Atherinops</i>	1	31.0	59.2	41.4-84.6
	2	50.3	86.2	68.6-108.3
	3	89.8	103.5	85.5-125.2
<i>Macrocyctis</i>	1	16.4	89.1	80.9-93.3
	2	<13.6	86.6	72.4-96.5
	3	12.2	102.0 ^a	NC

Median-effect concentrations (MEC) are LC50 for *Macrocyctis*, EC50 for *Haliotis*, and LC50 for *Holmesimysis* and *Atherinops*.

NC = not calculated.

^aExtrapolated beyond actual data set by linear regression.

Singer *et al.*, *Environ. Toxicol. Chem.* 10:1367 (1991)



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Corexit 9527: PBCO WAF versus CEWAF

Table 2. Results of spiked-exposure toxicity tests using Prudhoe Bay crude oil alone and combined with Corexit 9527 (O:D ratio = 10:1)^a

Species/Endpoint	EC/LC50 (mg/L THC _{CT C30})					
	WAF			CEWAF		
	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3
<i>Haliotis</i>	Larval abnormality					
	>34.0 ^b	>46.99	>33.58	19.09 (18.90, 19.28)	32.70 (32.11, 33.30)	17.81 (17.65, 17.96)
<i>Holmesimysis</i>	96-h mortality					
	>34.68	>25.45	>28.55	10.54 (9.08, 12.25)	10.75 (9.45, 12.22)	10.83 (NA) ^c
<i>Atherinops</i>	Initial narcosis					
	11.31 (9.14, 13.99)	11.58 (10.51, 12.77)	15.90 (14.71, 17.18)	11.07 (10.16, 12.05)	>38.33	48.03 (40.57, 56.85)
<i>Atherinops</i>	96-h mortality					
	16.34 (14.57, 18.55)	40.20 (38.68, 41.45)	35.73 (37.37, 46.85)	28.60 (17.49, 46.76)	74.73 (62.30, 89.60)	34.06 (30.24, 38.37)
<i>Atherinops</i>	Initial narcosis					
	26.63 (24.82, 27.59)	>48.22	31.76 (14.65, 46.59)	>101.82	>140.97	>62.22

^a Data are median-effect concentration and 95% confidence limits

^b EC/LC50 estimated to be above highest test concentration

^c Confidence limits not reliably calculable

Singer *et al.*, *Archiv. Environ. Contam. Toxicol.* 34:177 (1998)

- In general, WAF was less toxic than CEWAF
- However, trend is reversed for narcosis
- Toxicity is species, life stage and endpoint specific



where knowledge meets need...

Corexit 9500

- Toxicity of Corexits 9527 and 9500 was similar for abalone, but not for mysids
- Toxicity also depends on specific formulation and exposure conditions
- *What about the chemistry used to measure endpoints?*

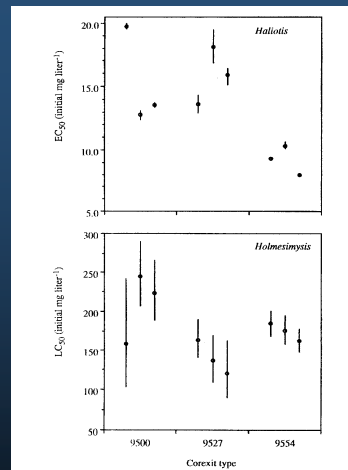
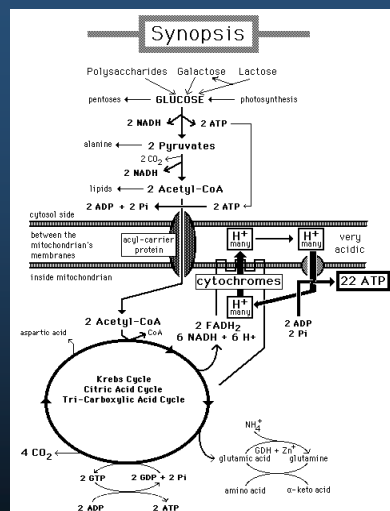


FIG. 5. Comparison of median-effect concentrations of triplicate *Haliotis* (top) and *Holmesimysis* (bottom) toxicity tests using Corexit 9500, 9527, and 9554. Data symbols represent EC_{50} with 95% confidence intervals.

Singer *et al.*, *Ecotoxicol. Environ. Saf.* 35:183 (1996)

III. Metabolomics – WAF vs CEWAF

- Assess actions of WAF vs CEWAF of PBCO in fishes under spiked- exposure conditions
- Apply $^1\text{H-NMR}$ -based metabolomics to demonstrate *very sensitive* sublethal actions on metabolism and amino acid balance



CROSERF Methods



WAF Exposures



CEWAF Exposures

Singer *et al.*, *Mar. Pollut. Bull.* 40:1007 (2000)

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Traditional Comparative Toxicity

- Total petroleum hydrocarbons (TPH; C₁₀ – C₃₆); GC-FID
- Volatiles (BTEX; C₆-C₉); purge-and-trap GC-MS
- Total hydrocarbon content (THC; C₆-C₃₆) – BTEX + TPH
- Spiked exposures confirmed via THC

Fish Species	WAF 96-h LC50	CEWAF 96-h LC50
Salmon Pre-Smolts	7.6 mg/L THC	48.6 mg/L THC
Salmon Smolts	7.5 mg/L THC	156 mg/L THC
Topsmelt Adults	> 3.4 mg/L THC	56.4 mg/L THC

Lin *et al.*, *Aquat. Toxicol.* 95:230 (2009)

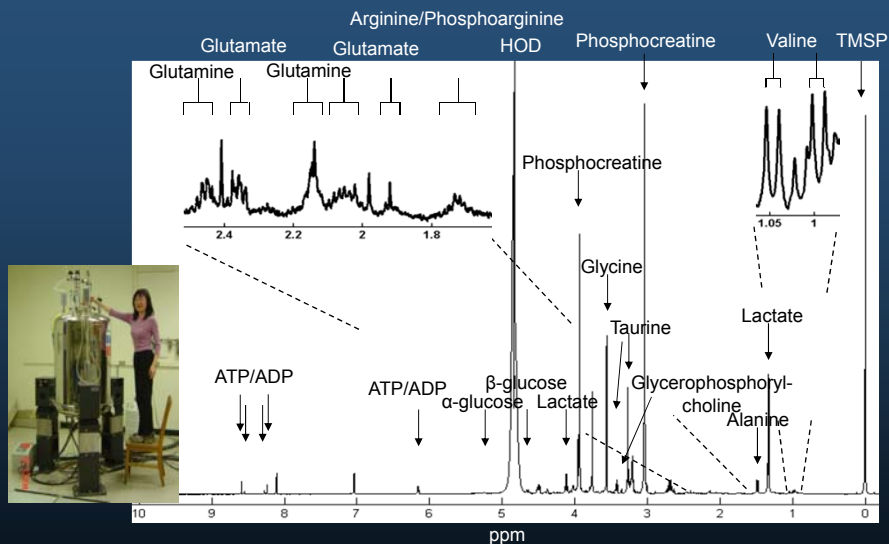
Van Scoy *et al.*, *Ecotoxicol. Environ. Saf.* 73:710 (2010)

Van Scoy *et al.*, *Ecotoxicol. Environ. Saf.* 78:99 (2012)

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NMR Spectrum of Muscle Extract



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Similar Changes in Profiles – *Topsmelt*

Metabolites	96 h		78 d	
	WAF	CEWAF	WAF	CEWAF
Valine	↑	↑	↓	↑
Lactate	↓	↓	↑	↑
Alanine	↑	↑	↓	↓
Arginine/Phosphoarginine	↑	↓	↓	↓
Glutamine	↑	↑	↓	↓
Succinate	↑	↑	↓	↓
Phosphocreatine	↓	↓	↑	↓
Taurine	↑	↑	↓	↓
Glycine	↑	↓	↑	↑
AMP	↓	↓	↓	↓
Histidine	↓	↓	↓	↓
ATP/ADP	↓	↓	↓	↓

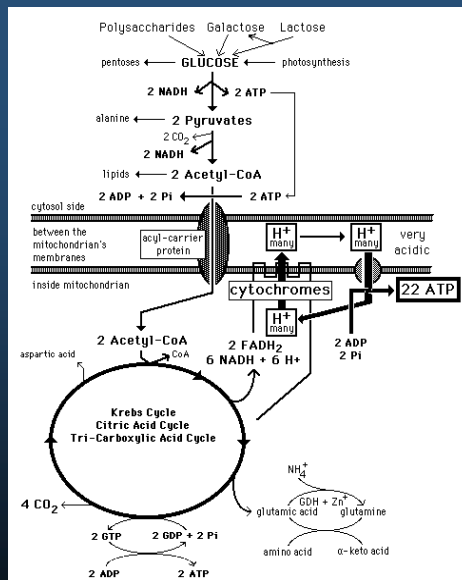
Van Scoy *et al.*, *Ecotoxicol. Environ. Saf.* 78:99 (2012)

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Implications

- WAF and CEWAF *both* increased free amino acids
- Ala, Arg, Gln, Glu, Val may result from proteolysis – or may be diverted from intermediary metabolism for new protein synthesis
- Diversion may reduce ATP available for development



Why are WAF and CEWAF Actions Similar?

- LC50s, based on THC (*dissolved + particulate*) were very different: WAF, 7.5 mg/L; CEWAF, 156 mg/L (salmon)
- However, toxicity may result from “bioavailable” (dissolved) fractions – not THC
- Hypothesis – *dissolved fractions produced in WAF and CEWAF are not significantly different*
- Tested with triolein-filled semi-permeable membrane devices (SPMDs)

IV. Chemistry and Bioavailability

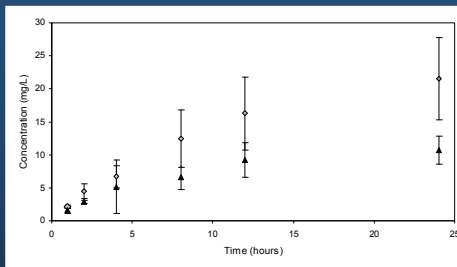
- CROSERF WAF and CEWAF
- Constant exposure – one SPMD removed at 1, 2, 4, 8, 12, 24 h
- Collect dissolved fraction via dialysis with hexane
- Analysis via GC-MS



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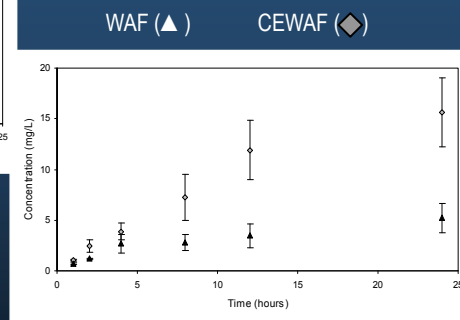
where knowledge meets need...

SPMD Results



Naphthalene WAF vs CEWAF

- Dissolved concentrations similar in first few hours (usual spiked period)



1-Methylnaphthalene WAF vs CEWAF

Van Scoy *et al.*, *Environ. Sci.: Processes Impacts* 15:2016 (2013)



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Conclusions

- Dispersants are one of several tools
- WAF and CEWAF toxicity depends on species, life stage, exposure, endpoint *and chemical analysis*
- Corexit 9500 decreases oil lethality to fishes some 7 to 20-fold – *based on total hydrocarbons*
- Similar metabolic impacts are possibly due to similar bioavailable fractions – *dependent on analysis*
- *Thus, use care in comparing literature values*







Dispersants U.S. Coast Guard Perspective

Michael Sams
Eighth Coast Guard District
Incident Management & Preparedness Advisor
Regional Response Team 6 Co-Chair

26 Jan 2014

1 of 4



Deepwater Horizon

- Dispersants were effective
- Critical tool in tool box
- Superb teamwork...political influence

2 of 4



Questions

- **How 'bad' was it**
- **Future options (products & monitoring)**
- **Public opinion**




3 of 4



New Frontiers

- **Updating our processes**
- **Refine aerial; explore subsea**
- **Capping stack; US-Mexico drilling**

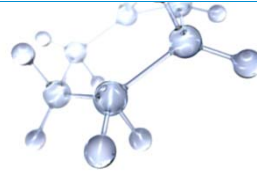
4 of 4



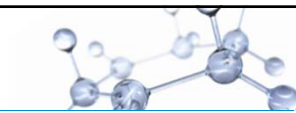
Michael Sams
Eighth Coast Guard District
Incident Management & Preparedness Advisor
(c) 281-881-6193
Michael.K.Sams@uscg.mil

5 of 5

Oil Spill Response: Dispersants



Spill Response Toolbox



**Mechanical Recovery:
Booms & Skimmers**



In-Situ Burning



Monitor & Evaluate

Aerial



**Dispersants
Vessel**

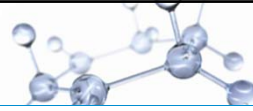


Subsea

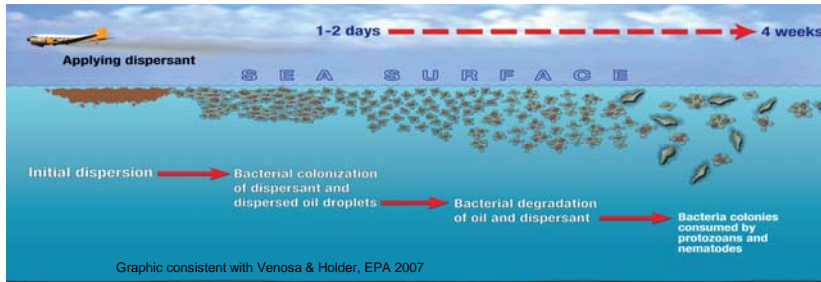


*The goal is to design a response strategy based on
Net Environmental Benefit Analysis (NEBA)*

Dispersants – What do they do?



- Dispersants are solutions of surfactants that reduce oil-water interfacial tension allowing slicks to disperse into very small droplets with minimal energy, enhancing the natural biodegradation process



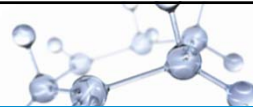
- Dispersed oil rapidly dilutes to concentrations <1 ppm within hours
- Dilution allows biodegradation to occur without nutrient or oxygen limits

3

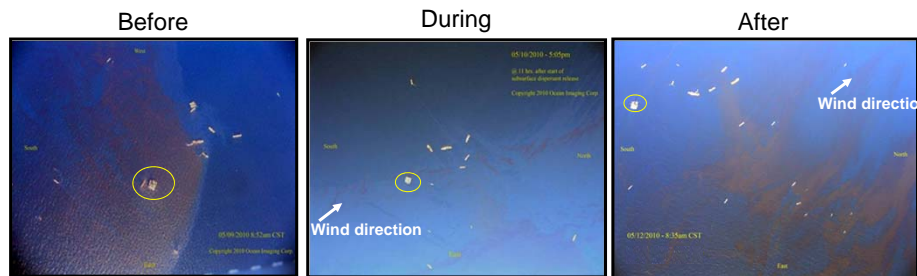
ExxonMobil
Research and Engineering

Subsea Dispersant Injection

May 9-10, 2010 Test



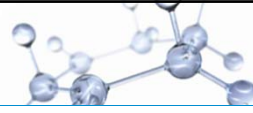
- Dispersant was injected near the spill source
- Allowed for targeted application with very high “encounter rate”
- Provided evidence of effectiveness and support for continued use



4

ExxonMobil
Research and Engineering

Summary and Future Work



- Dispersant use may present significant advantages over the limitations of mechanical recovery and should be considered as a primary response tool
- Subsea injection is a step-change advance that may reduce spill impacts by an order of magnitude
- Industry continues to work on optimizing subsea injection, new methods of application, and new products



Lessons Learned from DWH about Dispersants

- Dispersants work for their intended purpose; reducing shoreline impacts from a spill.
- Subsea dispersant use is a valuable tool in the responder's toolbox IF IT IS NEEDED.
- Dispersant use is a very complex and politically contentious issue at all levels of government (Federal, State, Local).



Questions That Remain?


- Subsea ecological impacts still remain to be fully understood.
- Will they ever be used again?
- How can science & technology help in the decision-making process?



New Frontiers with Respect to Dispersant Use?

- Nanotechnology holds promise as a potential alternative to chemical dispersants
- Chem/Phys/Bio/Geo studies need to continue.
- Science-Driven Spatial Technology will assist in decision-making.






**Consortium for the Molecular Engineering
of Dispersant Systems**

C-MEDS Mission

- To develop fundamental science that can be translated to applications in oil spill remediation. (GOMRI Theme IV)
- Adoption of technology developments to the portfolio of industrial and spill-response practice.
- Workforce development. To provide opportunities for students to develop fruitful scientific careers, for researchers to do work of impact and relevance.
- To conduct education and outreach activities that will be of service to the community in SE Louisiana, the Gulf Coast, and to the nation.



Specific Questions addressed by C-MEDS Research

1. What are the dynamics of events at the oil-water interface upon the addition of dispersants?
2. Can modern scientific tools in spectroscopy, electron microscopy, scattering, microfluidics etc. enable a detailed understanding of molecular events at the oil-water interface?
3. Can chemical computation and molecular simulations be utilized to better understand dispersant behavior and guide new dispersant development?
4. Are there new classes of environmentally benign dispersants that could be developed based on biopolymers, biosurfactants, interfacially stabilized particles? Can the physics of naturally occurring phenomena (oil-mineral aggregates, marine snow) enable the design of dispersants?
5. Can we design new systems and methods of delivery that minimize solvent and can be tuned to varying environmental conditions?



Novel Dispersant Technologies

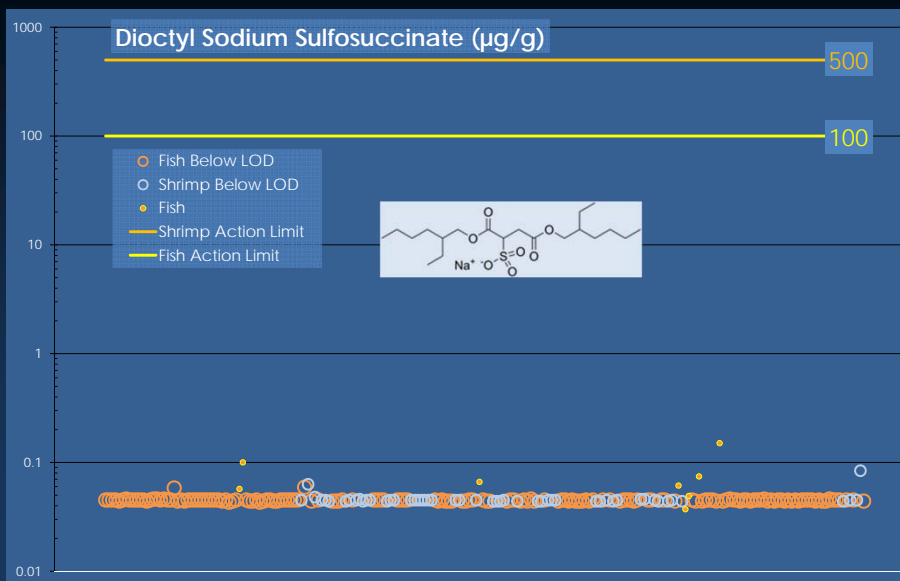
- **High efficiency dispersants at low concentrations (nano and micro particles, particle/surfactant systems, polymer grafted nanoparticles, polysoaps)**
- **Green and natural dispersants (low toxicity, biodegradable, nutrient loaded) polymers, particles, surfactants, fungal proteins.**
- **Dispersants that adhere and mix with oils.**
- **Herders and gelators to recover or burn oil.**
- **Imaging agents for dispersed oil (magnetic).**
- **Capsules/microgels for controlled release of dispersants.**

Corexit® Ingredients

Ingredient Name	CASRN	Common Uses	BCF/BAF	Rodent p.o. LD ₅₀
2-Butoxyethanol	111-76-2	Soaps, cosmetics and personal care products ≤ 10% Also, lacquers and paints, agricultural chemicals Indirect & Direct Food Additive: 21 CFR 175.105(FAP 1B0233); 178.1010(FAP 4A1375); +++	2 - 3	0.2–12 g/kg
Propylene Glycol	57-55-6	Drugs, cosmetics and personal care products Food products (GRAS): 21 CFR 175.105(FAP 1B0233, 2B0650); 178.3300; 175.300; 175.320; 177.2420; +++	< 10	18-46 g/kg
Dipropylene glycol monobutyl ether	29911-28-2	Cleaners, degreasers, paints, plasticizers	< 10	3-5 g/kg
Diocetyl sodium sulfosuccinate	577-11-7	OTC Laxatives, cosmetics Indirect & Direct Food Additive: 21 CFR 73.1; 131.130; 133.124; ++++	< 10	2.6-5.7 g/kg
Petroleum distillates	64742-47-8	Paints, varnishes, lubricants (e.g. HW-40), hand-cleaners (e.g. Mojo & Goop); C-8 to C-20 Aliphatic HC; Norpar-13 (CASRN 94094-93-6) is Food-Grade	60 - 80	> 5g/kg
Span 80	1338-43-8	Cosmetics & personal care products Drugs and parenteral products		
Tween 80	9005-65-6	Food Products: 21 CFR 73.1; 107.105; 172.515; 172.623; ++++	36 - >300	NOAEL >5 g/kg d
Tween 85	9005-70-3			

FDA approval means that the compound is safe for its approved uses and the human exposures associated with those uses


DOSS in Gulf seafood






▶ IMPACTS VS. EFFECTIVENES

- Do we know the trade-offs?
- Dispersants effective at the wellhead, surface?
- Empirical data on efficacy, impacts need to be accessible




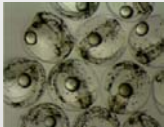



(Fingas, 2013)

 Ocean Conservancy © 2013 Ocean Conservancy

▶ IMPACTS: MORE QUESTIONS

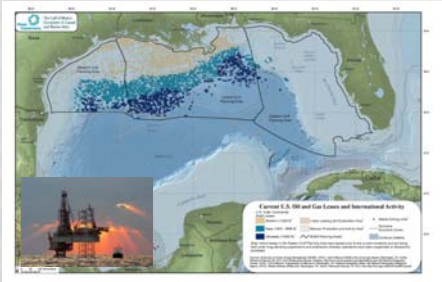

- More harmful combined w/ oil than by itself?
- Concerns about toxicity to organisms remain
- Predict, monitor impacts to biota, food web?

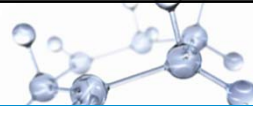
Ocean Conservancy © 2013 Ocean Conservancy

▶ IMPACTS: GOING FORWARD

- O & G production trending deeper
- Address research gaps, improve monitoring
- Improve transparency of data, results

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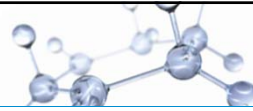


Impacts/Recovery/Restoration

1

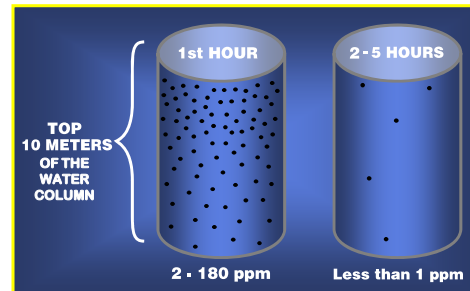
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Research and Engineering

Environmental Impacts



• Toxicity

- Rapid dilution limits ecosystem impacts of both dispersant and dispersed oil, i.e., concentrations start low and decrease quickly
- Many studies use high constant concentrations and long exposures
- Lab toxicity tests should reflect real world exposures, e.g., protocols developed by Chemical Response to Oil Spills: Ecological Research Forum (CROSERF)



Lessard, R.R. and DeMarco, G. (2000) The significance of oil spill dispersants. *Spill Science & Technology Bulletin*, 6, 59-68


2

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Research and Engineering

Human Health

- Modern dispersants use ingredients found in many household products
 - NALCO website*
- Following proper application procedures is important
- Test results for dispersants in Gulf seafood indicated very low levels of concern, "There is no question Gulf seafood coming to market is safe from oil or dispersant residue."

(http://www.noaa.gov/stories/2010/20101029_seafood.html)



Corexit® 9500 Ingredients	Common Day-to-Day Use Examples
Span™ 80 (surfactant)	Skin cream, body shampoo, emulsifier in juice
Tween® 80 (surfactant)	Baby bath, mouth wash, face lotion, emulsifier in food
Tween® 85 (surfactant)	Body/Face lotion, tanning lotions
Aerosol® OT (surfactant)	Wetting agent in cosmetic products, gelatin, beverages
Glycol butyl ether (solvent)	Household cleaning products
Isopar™ M (solvent)	Air freshener, cleaner

*<http://www.nalco.com/applications/corexit-technology.htm>


3

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Relative Toxicity

- It's important to frame the discussion in a balanced fashion
- Potential risks need to be understood

Environment Canada Study



<u>Product</u>	<u>Toxicity (ppm)</u>
Palmolive® Dish Soap	13
Sunlight® Dish Soap	13
Mr. Clean®	30
Corexit® 9500	350

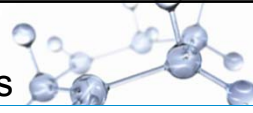
(96 HR Rainbow Trout LC50)

↓
Less toxic

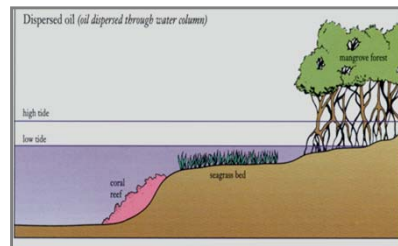
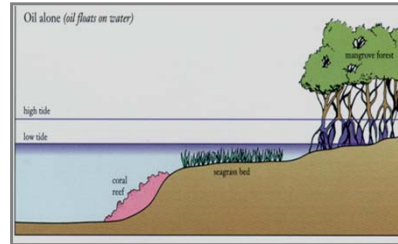
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Net Environmental Benefit Analysis



- It's important to consider potential tradeoffs during a spill response decision making process
- The goal is to minimize negative consequences
- Spills are different and all response options should be considered

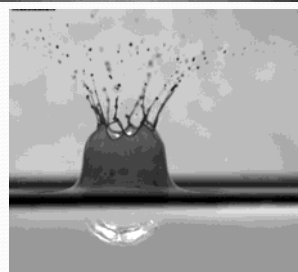
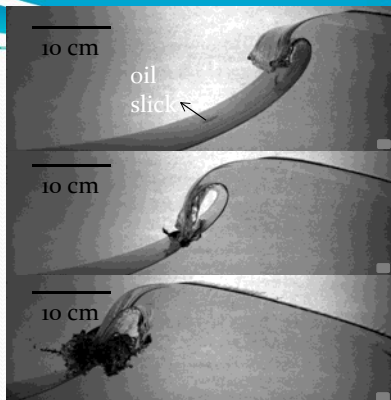


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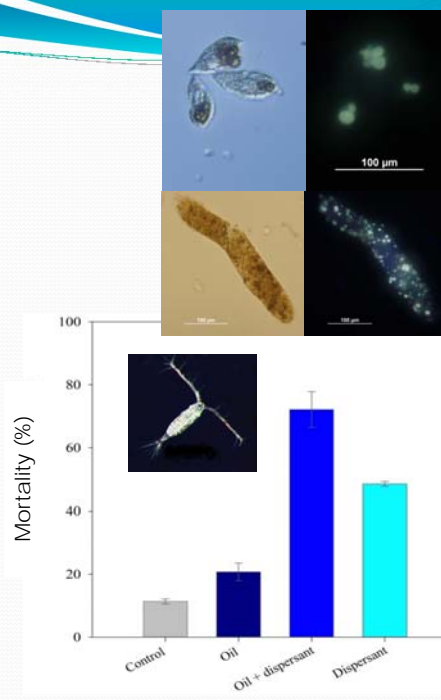
Physical processes enhance breakup of oil treated with dispersants

- surface waves and rain drops striking oil slicks produce micron sized droplets in air and water
- Biological activity such as feeding currents and swimming behavior also break up dispersant treated oil
- Aerosols may be health hazard to humans and wildlife



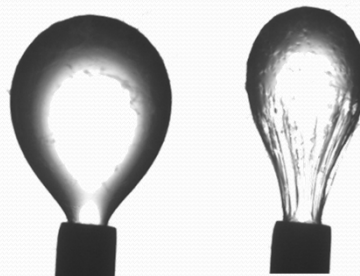
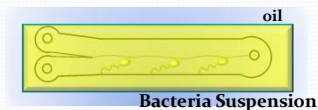
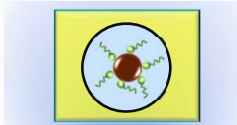
Dispersed oil: Protozoa and copepods ingest small oil droplets

- Dispersed oil in size range of food for zooplankton, and readily consumed by protozoa and metazoans
- Ingested toxic PAHs readily absorbed and concentrated in crustacean zooplankton
- Volume of oil where toxic thresholds exceeded relatively small, and zooplankton reproduce rapidly



Smaller drops rise slowly and degrade faster

- More surface area for loss of soluble compounds
- More surface area for bacterial colonization – studies of chemotaxis of oil degrading bacteria using microfluidics and holography
- Bacterial films modify surficial properties of oil droplets

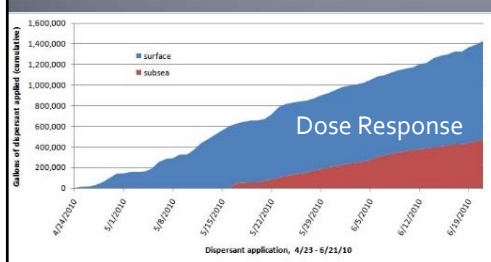




Risk & Oil Dispersants & Human Health

James P. Fabisiak, Ph.D.
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Graduate School of Public Health
University of Pittsburgh, Pittsburgh PA

Four Steps of Risk Assessment

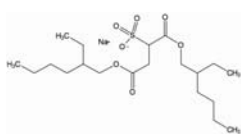


Hazard Identification

Product	Ingredients
BIODISPERS (Petrotech America)	Proprietary
JD-309 (GlobeMark Resources Ltd.)	Proprietary
JD-2000 (GlobeMark Resources Ltd.)	Proprietary
NOKOMIS 3-AA (Mar-Len Supply, Inc.)	Proprietary
NOKOMIS 3-F4 (Mar-Len Supply, Inc.)	Proprietary
COREXIT 9500 (Nalco Energy Services)	Sorbitan, mono-(2)-9-octadecenoate Sorbitan, mono-(2)-9-octadecenoate, poly(oxy-1,2-ethanediyl) deriv. Sorbitan, tri-(2)-9-octadecenoate, poly(oxy-1,2-ethanediyl) deriv. Butanedioic acid, sulfo-, 1,4-bis-(2-ethylhexyl) ester, sodium salt (Diocetyl sodium sulfosuccinate) (10 – 30%) 1-(2-butoxy-2-methylethoxy)-2-propanol (1 – 5%) Distillates (petroleum), hydrotreated light (10 – 30%)
COREXIT 9527 (Nalco Energy Services)	Sorbitan, mono-(2)-9-octadecenoate Sorbitan, mono-(2)-9-octadecenoate, poly(oxy-1,2-ethanediyl) deriv. Sorbitan, tri-(2)-9-octadecenoate, poly(oxy-1,2-ethanediyl) deriv. Butanedioic acid, sulfo-, 1,4-bis(2-ethylhexyl) ester, sodium salt (Diocetyl sodium sulfosuccinate) (10 – 30%) 1-(2-butoxy-2-methylethoxy)-2-propanol (1 – 5%) Distillates (petroleum), hydrotreated light 2-Butoxy-ethanol (30 – 60%)
MARE CLEAN 200 (Taiho Industries Co. Ltd.)	Poly(oxy-1,2-ethanediyl), α -hydro- ω -hydroxy-, ether with 1,2,3-propanetriol (2)-9-octadecenoate Poly(oxy-1,2-ethanediyl), α -(2)-1-oxo-9-octadecen-1-yl- ω -hydroxy- Poly(oxy-1,2-ethanediyl), α -(2)-1-oxo-9-octadecen-1-yl- ω -(2)-1-oxo-9-octadecen-1-yl-oxy- (Polyethylene Glycol Diolate) Sorbitan, tri-(2)-9-octadecenoate, poly(oxy-1,2-ethanediyl) deriv. (Polysorbate 85) Alkanes, C ₁₄ -30

DISPERSIT SPC 2000 (U.S. Polychemical Corp.)	Poly(oxy-1,2-ethanediyl), α -(2)-1-oxo-9-octadecen-1-yl- ω -hydroxy Ethoxylated Amines, tallow alkyl N,N-bis(hydroxyethyl)-Amides, coco Ethoxylated Alcohols, C ₁₂₋₁₄ -secondary, 1(or 2) - (2-methoxymethylethoxy) - propanol
SAF-RON Gold (Sustainable Environmental Technologies, Inc.)	Proprietary
NEOS AB3000 (Neos Company, Ltd.)	Proprietary
SEA BRAT 4 (Alabaster Corp.)	Proprietary

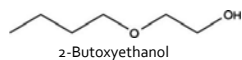
Dose-Response



Diocetyl sodium sulfosuccinate



Typical dose is 100 – 250 mg/day.



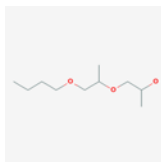
2-Butoxyethanol



Causes red blood cell damage in some animals, however, humans are significantly more resistant.

[Ambient] \approx $\mu\text{g}/\text{m}^3$
[Occupational] \approx mg/m^3

Some report irritation of the nose and eyes, headache, a metallic taste, or vomiting at 480 mg/m^3 at 4-8 hrs.

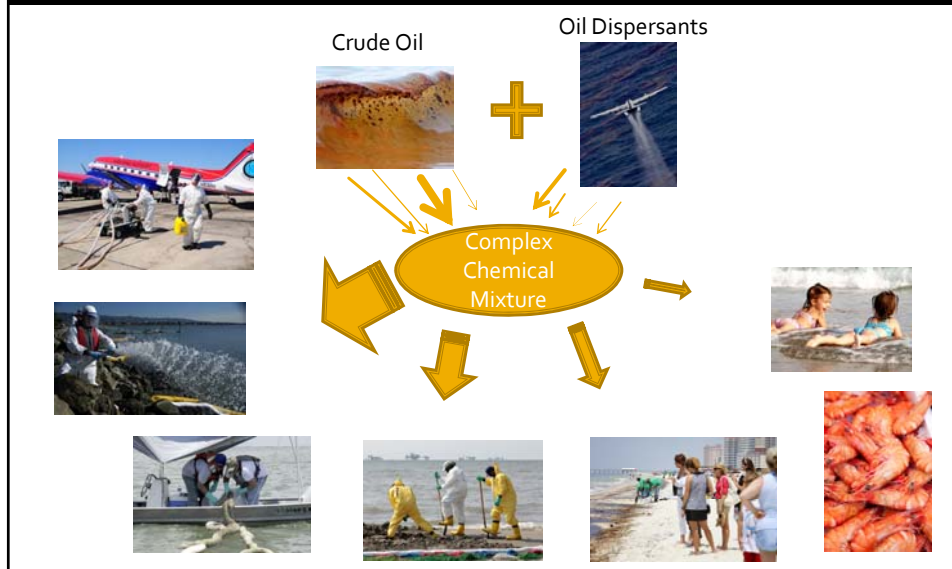


Dipropylene glycol butyl ether



Mostly used in production of industrial grade solvent products. In general, P-series glycol ethers are considered safer alternatives to E-series (ie. 2-butoxyethanol)

Exposure Assessment



Risk Characterization

- Dispersant risk during spill
 - Occupational > General Population
 - Moderate – Minimal
- Several ongoing health studies in the Gulf Region
 - Assessing exposure will be a big challenge.
- Do dispersants affect distribution, exposure, and toxicity of oil?
 - DSS is considered as a possible way to enhance drug delivery.
- Residual present-day effects – *Probably very low.*
 - Assuming $\approx 10\%$ of Gulf was affected by DWH spill and then mixed with total volume of dispersant used, one would need to drink about 3 million gallons to get the amount of DSS contained in one dose of stool softener.

