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Monitoring Subsurface Oil released from Deepwater Horizon MC 252 in the Gulf of Mexico
Centre for Offshore Oil, Gas and Energy Research (COOGER)

• Primary role is research to assess the risks from offshore oil and gas and ocean renewable energy activities and to develop mitigation technologies

• Identification of R&D needs

• National coordination of regional expertise and infrastructure

• Provision of scientific support for decision making for policy and regulations

• Promote national / international research collaborations with other government agencies, industry and academia
Offshore Environmental Impacts

Assessment of environmental impacts and risks associated with exploration, production and transport operations

Primary program focus:

- Drilling wastes
- Produced water
- Seismic impacts
- Assessment of oil spill impacts and remediation

A balanced multidisciplinary research program that maintains expertise to enable response to future environmental issues
DFO Oil Spill Countermeasure Research

By the conduct of laboratory, mesocosm and “controlled oil spill” experiments in the field, DFO developed oil spill countermeasure technologies (bioremediation, phyto-remediation and surf-washing) and methodologies to quantify habitat recovery.
There is no single response technique that is suitable for all circumstances

Oil spill responses:
- Booming and skimming
- *In-situ* burning
- Bioremediation
- Chemical dispersion

At open sea, dispersant use attracts most attention due to restrictions to other methods
Dispersant (surfactant)

Hydrophilic

Hydrophobic

Surfactant-stabilized oil droplet (micelles)

Activity of Chemical Dispersants

Dispersant sprayed onto oil slick

Surfactant locates at interface

Oil slick broken into droplets by mixing energy

The droplets dispersed by turbulence leaving low oil concentrations

Surfactant reduces the oil-water interfacial tension by orienting the interaction of hydrophilic groups with the water phase and the hydrophobic groups with oil.

Reduced oil-water interfacial tension facilitates the formation of a large number of small oil droplets that can be entrained in the water column.
### Chemical Constituents (Dispersant – Corexit)

<table>
<thead>
<tr>
<th>CAS #</th>
<th>Name</th>
<th>Common Day-to-Day Use Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1338-43-8</td>
<td>Sorbitan, mono-(9Z)-9-octadecenoate</td>
<td>Skin cream, body shampoo, emulsifier in juice</td>
</tr>
<tr>
<td>9005-65-6</td>
<td>Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs.</td>
<td>Baby bath, mouth wash, face lotion, emulsifier in food</td>
</tr>
<tr>
<td>9005-70-3</td>
<td>Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs.</td>
<td>Body/Face lotion, tanning lotions</td>
</tr>
<tr>
<td>577-11-7</td>
<td>* Butanediolic acid, 2-sulfo-, 1,4-bis(2-ethylhexyl) ester, sodium salt (1:1)</td>
<td>Wetting agent in cosmetic products, gelatin, beverages</td>
</tr>
<tr>
<td>29911-28-2</td>
<td>Propanol, 1-(2-butoxy-1-methylethoxy)</td>
<td>Household cleaning products</td>
</tr>
<tr>
<td>64742-47-8</td>
<td>Distillates (petroleum), hydrotreated light</td>
<td>Air freshener, cleaner</td>
</tr>
<tr>
<td>111-76-2</td>
<td>** Ethanol, 2-butoxy</td>
<td>Cleaners</td>
</tr>
</tbody>
</table>

* Contains 2-Propanediol

** Ethanol, 2-butoxy-) is absent in the composition of COREXIT 9500
Enhanced Dispersion for Oil Spill Response

• Based on the concept of transferring oil from the sea surface into the water column, as small oil droplets

• These are diluted by natural processes to concentrations below toxicity threshold limits

• Dispersed oil droplets are degraded more rapidly by natural bacteria

• Achieved with chemical oil dispersants and/or facilitation of oil mineral aggregate formation
Uncertainties remain high regarding dispersant use at sea

- Dispersant efficacy at different sea states is not clear
- Biological effects of dispersed oils are poorly understood

National Research Council (NRC) Committee on Understanding Oil Spill Dispersants: Efficacy and Effects (2005) Identified two factors to be addressed in oil dispersant efficacy studies:

- Energy dissipation rate (turbulence/sea state conditions)
- Particle size distribution and mass balance

To address this issue, a wave tank facility was constructed by Fisheries and Oceans Canada (DFO) and the U.S. Environmental Protection Agency (EPA)
BIO Wave Tank

- Tidal current simulation by vertical manifolds along the sides of the tank
- Reproducible waves produced (of known energy dissipation rate), including breaking waves, at precise locations along length of tank
- Development of experimental protocols and instrumentation to monitor dispersed oil in the water column
**Oil Droplet Size Distribution**

**LISST Particle Size Analysis**

**- Dispersant**

- Mean Diameter (µm)
  - 10
  - 100

- Particle Concentration (µL/L)
  - 0.0
  - 0.5
  - 1.0

- Times:
  - t = 1 min
  - t = 10 min
  - t = 30 min
  - t = 60 min

**+ Dispersant**

- Mean Diameter (µm)
  - 10
  - 100

- Particle Concentration (µL/L)
  - 0.0
  - 0.5
  - 1.0

- Times:
  - t = 1 min
  - t = 10 min
  - t = 30 min
  - t = 60 min

- Dispersant
- + Dispersant
Dispersant Activity

Extracted images from cinematic digital holography of turbulent break-up of crude oil mixed with dispersants into microdroplets

UV Fluorescence of Oil in Seawater

When a relatively high concentration of MC 252 crude oil (650ppm) is subject to UV excitation at 280nm:

- Emission fluorescence is primarily located in a peak centered at 340nm in the absence of dispersant (DOR 0)
- Addition of Corexit 9500 at a DOR of 1:20 shifts emission to a large, broad peak centred at 450 nm
Fluorescence Intensity Ratio (FIR)

Emission at 340nm is divided by emission at 450nm

Oils dispersed on their own (with dispersion efficiencies of < 20%), were associated with FIRs > 4, while chemically dispersed oils (with efficiencies > 40%) were associated with FIRs < 4

FIR was a potential method to quickly assess whether an oil slick had been sufficiently dispersed (SMART Tier II)
Gulf of Mexico Oil Spill

Deepwater Horizon MC-252 oil spill - largest accidental marine oil spill in the history of the petroleum industry

- April 20, 2010 - explosion on the Deepwater Horizon drilling rig killed 11 platform workers and injured 17 others

- July 15, 2010 - leak was stopped by capping the wellhead which had released 4.9 million barrels of crude oil

- September 19, 2010 - federal government declared the well "effectively dead" after successful completion of the relief well
DWH Oil Spill Peak Statistics

• 4.9 million bbls of oil discharged
• 1.8 million gallons of dispersants used
• 411 in-situ burns conducted (265,450 bbls of oil burned)
• 48,200 responders
• 9,700 vessels (6,500 government owned)
• 127 surveillance aircraft
• 3.8 million ft of hard boom deployed
• 9.7 million ft of soft boom deployed
Encounter Rate is Key to Offshore Response

Courtesy of Ocean Imaging
Application of Oil Dispersants - GoM

- Based on discharge rates - final estimate of 53,000 barrels per day (8,400 m³/d) - each day the Gulf of Mexico Oil Spill would be considered a major incident.

- In addition to mechanical recovery techniques (skimming and booming) and in situ burning, oil dispersants were used to prevent landfall of the oil in the Deepwater Horizon Spill.

- Beginning in early May responders began injecting dispersants at the source of the release (~1500m depth) to reduce oil from reaching the surface.
  - Advantages of subsurface injection:
    - Reduced VOCs (volatile organic compounds)
    - Reduced Oil Emulsification
    - Volume of dispersant needed
Dispersant Application on the Sea Surface

- Dispersant was applied from vessels by spraying when VOC levels near the source site reached unacceptable levels, enabling work to continue on the drilling and containment rigs/vessels.
Subsurface Injection of Dispersants
Cumulative Dispersant Use

* 4,200,000 L of dispersant added by subsurface injection
Plume Monitoring and Assessment for Subsurface Dispersant Application

**PART 1:** “Proof of Concept” to determine if subsurface dispersant operation is chemically dispersing the oil plume.

Following review by the RRT….

**PART 2:** Robust sampling to detect and delineate the dispersed plume based on the results of PART 1 and input from hydrodynamic modeling

DFO COOGER was requested by US EPA to provide scientific expertise to implement the directive

All data provided to the United States Coast Guard (USCG) Federal On-Scene Coordinator, and the Environmental Protection Agency (EPA) Regional Response Team (RRT)
## DFO Sampling Effort

<table>
<thead>
<tr>
<th></th>
<th>Person Days</th>
<th>Stations</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>May</strong></td>
<td>91</td>
<td>68</td>
<td>1020</td>
</tr>
<tr>
<td><strong>June</strong></td>
<td>136</td>
<td>107</td>
<td>1674</td>
</tr>
<tr>
<td><strong>July</strong></td>
<td>136</td>
<td>65</td>
<td>1060</td>
</tr>
<tr>
<td><strong>August</strong></td>
<td>143</td>
<td>92</td>
<td>1439</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>506</strong></td>
<td><strong>320</strong></td>
<td><strong>5193</strong></td>
</tr>
</tbody>
</table>

* Cost recovery from the U.S. Government with BP as the responsible party accountable for all cleanup costs

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R/V Ocean Veritas

R/V Brooks McCall
Dispersant Monitoring and Assessment for Subsurface Dispersant Application

- US EPA and USCG directives required BP to implement a monitoring and assessment plan for subsurface and surface use of dispersants
  - Shutdown Criteria
    - Significant reduction in dissolved oxygen (< 2 mg/L)
    - Rotifer acute toxicity tests
- Later addenda to implement SMART Tier 3 Monitoring Program
  - Droplet size distribution (LISST)
  - CTD instrument equipped with CDOM fluorometer
  - Discreet sample collection to measure fluorometry (FIR)
  - Aim to eliminate surface application altogether with subsea dispersant addition limited to < 15,000 gpd
Joint Analysis Group (JAG)
Surface and Subsurface Oceanographic, Oil, and Dispersant Data

• Working group of scientists from EPA, NOAA, OSTP, BP and DFO
• Analyze an evolving database of sub-surface oceanographic data by BP, NOAA, and academic scientists
• Near term actions:
  • Integrate the data
  • Analyze the data to describe the distribution of oil and the oceanographic processes affecting its transport
  • Issue periodic reports
DFO Station Locations

Total of 320 Stations
Small particles (2.5 - 60µm) were indicative of oil droplets in the subsurface plume.
Sub-surface Oil Profiles
## Oil Chemistry Results

### All Depths

<table>
<thead>
<tr>
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<th>Number of Samples Analyzed</th>
<th>Summary of Samples &gt;LOD (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>&lt;LOD</td>
</tr>
<tr>
<td><strong>BTEX</strong></td>
<td>2743</td>
<td>2350 (86%)</td>
</tr>
<tr>
<td><strong>PAHs</strong></td>
<td>2307</td>
<td>1734 (75%)</td>
</tr>
<tr>
<td><strong>nAlkanes</strong></td>
<td>2304</td>
<td>2091 (91%)</td>
</tr>
</tbody>
</table>

### Bottom (>700m)

<table>
<thead>
<tr>
<th></th>
<th>Number of Samples Analyzed</th>
<th>Summary of Samples &gt;LOD (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>&lt;LOD</td>
</tr>
<tr>
<td><strong>BTEX</strong></td>
<td>1478</td>
<td>1164 (79%)</td>
</tr>
<tr>
<td><strong>PAHs</strong></td>
<td>1219</td>
<td>995 (82%)</td>
</tr>
<tr>
<td><strong>nAlkanes</strong></td>
<td>1219</td>
<td>1104 (91%)</td>
</tr>
</tbody>
</table>
Level and Trend in DO$_2$ Depressions

Total of 419 DO$_2$ profiles compared to annual mean climatology
Normalized Mean CDOM Fluorescence (1000-1300 m) vs. Distance from Wellhead
UV Fluorescence Analysis

- FIR only applicable at high oil concentrations (100’s of ppm)
  - Gulf of Mexico water samples were much lower (low ppm to ppb range)

- UV fluorescence can detect low concentrations of oil (excitation: 280nm / emission 340nm)

- Many of the fluorometers deployed during the Deepwater Horizon spill employed higher excitation and emission wavelengths
  - Instruments should be modified to lower wavelengths for detection of dispersed oil at low concentrations
3D Fluorescence Spectra: MC252 & BTEX

DFO/NOAA Fluorometry Workshop

- Chelsea Aquatrack
- Wetlabs Safire
- Wetlabs Eco
- Wetlabs EcoTriplet
- Turner C7
- Satlantic Suna
UV-Fluorescence

SPC & i340 vs. Distance from Wellhead

SPC: Surface (<10m)

SPC: Bottom (>700m)

i340: Surface (<10m)

i340: Bottom (>700m)
2-butoxyethanol, dipropylene glycol n-butyl ether (DPnB) was used to determine the expanse of the Deepwater Horizon dispersed oil and Corexit.

* USEPA chronic screening level = 1,000 µg/L
Fate of Dispersed Oil Droplets

Source: http://www.response.restoration.noaa.gov
Analysis of Near-field Oil Droplet Data
(JAG Analysis DFO Data: Dr. J.A. Galt, NOAA, HAZMAT)

- Within 15 km of the well and below 1000 m oil droplet concentrations (< 65 microns) were fully consistent with an essentially neutrally buoyant plume.

- The plume was filamentous, a significant fraction of the bottle casts missed it and thus exhibited little or no oil in droplet form. Significant non-zero sample results, assumed to be within the filaments, showed total droplet volumes in the 10 ppm range with a max observed value of 16 ppm.

- Observed values appeared to drop off by an order of magnitude within 10 km. If we use this as a rough scaling distance for the mixing and dilution of the oil droplet filaments or plume then we would expect to have total droplet concentrations reduced to the ppb level within about 40 km.

- Although this is a rough estimate it is consistent with the bulk of the available observations and by the time the droplets get 40 kilometers away numerous other physical and biological processes will start to alter the state and composition of the plume.
Fate of the Oil: GOM spill

Response estimates expressed as % cumulative volume of oil discharged in the best, expected, and worst cases

Oil Budget Calculator
October 2010
NOAA (National Oceanic and Atmospheric Administration)

Other: Remaining oil is at the surface as light sheen or weathered tar balls, biodegraded, or already came ashore

July 14, 2010 Response Estimate: Percentage of Total

- Best Case
  - Direct Recovery from Well Head: 17%
  - Naturally Dispersed: 13%
  - Evaporated or Dissolved: 20%
  - Chemically Dispersed: 29%
  - Burned: 6%
  - Skimmed: 4%
  - Other Oil: 11%

- Expected
  - Direct Recovery from Well Head: 17%
  - Naturally Dispersed: 13%
  - Evaporated or Dissolved: 23%
  - Chemically Dispersed: 16%
  - Burned: 5%
  - Skimmed: 3%
  - Other Oil: 23%

- Worst Case
  - Direct Recovery from Well Head: 16%
  - Naturally Dispersed: 12%
  - Evaporated or Dissolved: 25%
  - Chemically Dispersed: 10%
  - Burned: 5%
  - Skimmed: 2%
  - Other Oil: 30%
Future of Dispersant Use

• The ability to effectively deploy and monitor an unprecedented dispersant response in the GoM was based on the past decades’ improvements

• Misperceptions and knowledge gaps over their use remain. Areas for improvement include:
  • Need to be a common understanding of the risks and benefits of dispersant use, as well as the safety and effectiveness of dispersant products
  • Additional research is needed on the behavior and long term fate of dispersed oil in the water column when dispersants are applied at the sea floor
  • Conduct of field trials to advance and validate existing knowledge
  • Revision of IMO Guidelines for Chemical Oil Dispersant Use
Toxicity of Dispersants

Normal

Spinal Curvature

Pericardial & Yolk Sac Edema, Cranio-Facial Malformation

Spinal Curvature & Yolk Sac Edema
Wave tank Toxicity Studies

Hydrocarbon concentrations for Arabian light crude oil were not high enough to cause toxicity in Atlantic herring embryos.
GoM Spill Related Publications 2010-2011

Accepted (In Press):


Published:


