PERSISTENCE, FATE, AND EFFECTIVENESS OF DISPERSANTS USED DURING THE DEEPWATER HORIZON OIL SPILL

Monica Wilson, *Larissa Graham, Chris Hale, Emily Maung-Douglass, Stephen Sempier, and LaDon Swann*

The Deepwater Horizon (DWH) oil spill was the first spill that occurred in the deep ocean, nearly one mile below the ocean's surface. The large-scale applications of dispersants used at the surface and wellhead during the Deepwater Horizon oil spill raised many questions and highlighted the importance of understanding their effects on the marine environment.

Oiled waters in Orange Beach, Alabama. (NOAA photo)

Emergency responders used a large amount of dispersants during the 2010 DWH oil spill. They applied approximately 1.8 million gallons of chemical **dispersants** (Corexit 9527A and 9500A, referred to as Corexit in this document) to surface waters that were oiled from April 22 through July 19.[1] They also injected roughly 771,000 gallons of dispersants directly into the flow of oil and gas from the Macondo wellhead (Figure 1).[1,2] Before this event, scientists did not know how effective dispersants were when used in the deep ocean.[2,3] Most studies were based on sea surface spills and predicted where the oil would go and how long it would stay in the environment. Deep waters have higher pressures and lower temperatures that can cause dispersed oil to behave differently than it does on the surface.

THE SEA GRANT and GOMRI PARTNERSHIP

The mission of Sea Grant is to enhance the practical use and conservation of coastal, marine and Great Lakes resources in order to create a sustainable economy and environment. There are 33 university–based Sea Grant programs throughout the coastal U.S. These programs are primarily supported by the National Oceanic and Atmospheric Administration and the states in which the programs are located.

In the immediate aftermath of the Deepwater Horizon spill, BP committed $500 million over a 10–year period to create the Gulf of Mexico Research Initiative, or GoMRI. It is an independent research program that studies the effect of hydrocarbon releases on the environment and public health, as well as develops improved spill mitigation, oil detection, characterization and remediation technologies. GoMRI is led by an independent and academic 20–member research board.

The Sea Grant oil spill science outreach team identifies the best available science from projects funded by GoMRI and others, and only shares peer-reviewed research results.

Sea Grant
Texas • Louisiana • Florida
Mississippi-Alabama
http://gulfseagrant.org

GULF OF MEXICO RESEARCH INITIATIVE
http://gulfresearchinitiative.org

HOW DISPERSANTS WORK

Chemical dispersants break large oil slicks into small oil droplets. The smaller droplet size affects how the oil moves in the water and how it interacts with the environment. The natural processes that remove oil from the environment occur more easily when oil is in the form of small droplets. For example, ultraviolet light from the sun, evaporation, and bacteria that feed on oil can remove it from the water more easily when dispersants are used.[4] However, dispersants can accelerate the mixing of oil from the surface into the water column,[5] which increases marine life's exposure to the oil.[4]

PERSISTENCE OF DISPERSANTS

To understand how long dispersants remain in nearshore and offshore environments, scientists measured the concentration of **dioctyl sodium sulfosuccinate (DOSS)**.[2]

DOSS, or dioctyl sodium sulfosuccinate, is one of the ***surfactants*** *in Corexit 9527A and 9500A. DOSS, and other surface-active agents, lowers the tension between oil and water particles allowing them to mix* ***(emulsify)****. DOSS is a common ingredient in consumer products, such as detergents, cosmetics, and laxatives, and therefore, can end up in lakes, rivers, and coastal waters through stormwater runoff or our wastewater systems.*[6]

Nearshore waters

Nearly four years after the spill, scientists found DOSS in oiled samples collected on Gulf of Mexico beaches. Scientists collected tar balls and sand patties between June 2012 and January 2014 from Florida, Alabama, Mississippi, and Louisiana shores. DOSS was found in these samples. However, the amount of oil and DOSS in different samples was patchy and inconsistent

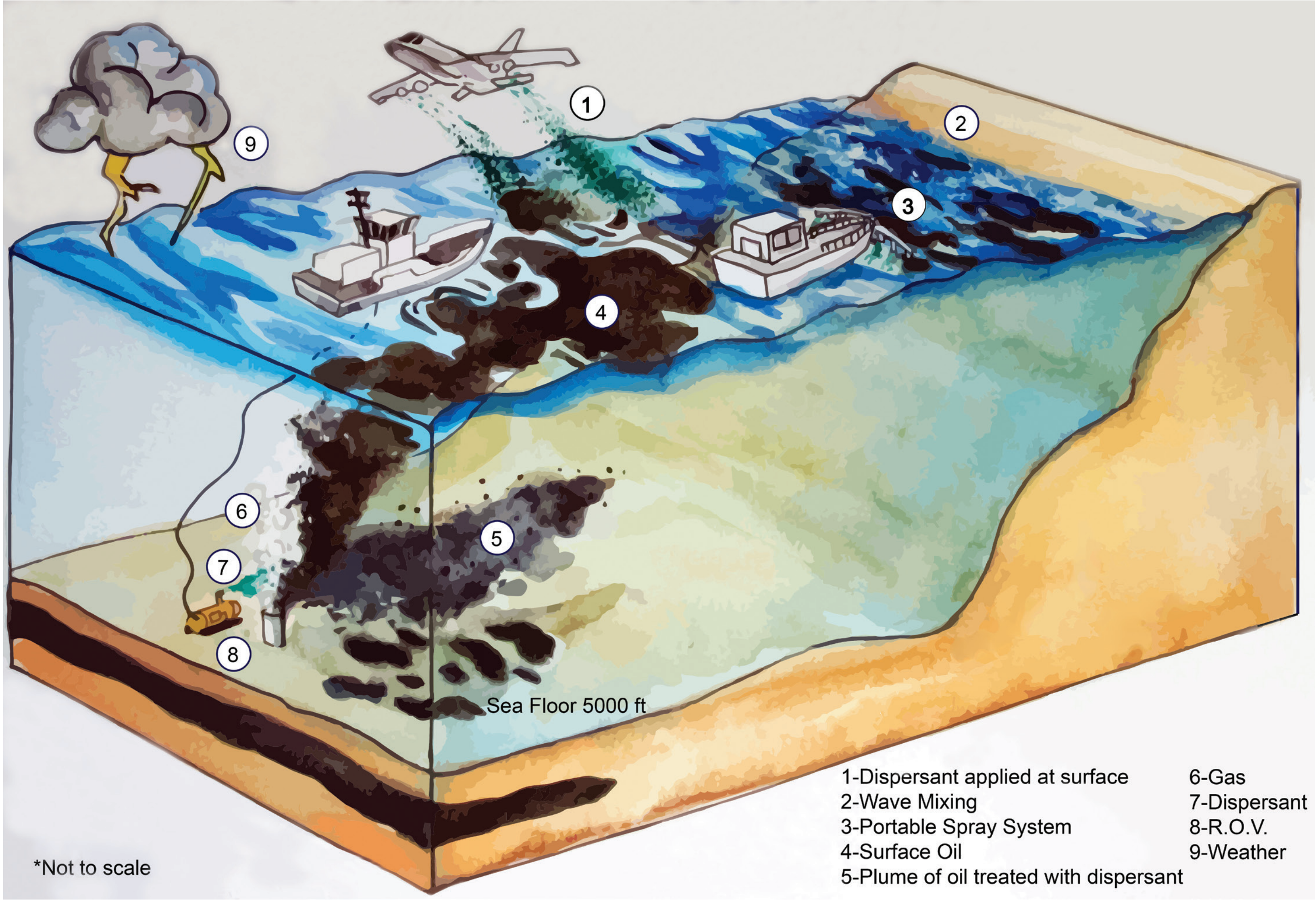


FIGURE 1. *Illustration showing the transport of the oil and how dispersant were applied during the Deepwater Horizon oil spill. (Florida Sea Grant/Anna Hinkeldey)*

because the oil washing up on the beach was from offshore oil mats.[7]

DOSS found in the nearshore environment is not always linked to the use of dispersants. Although scientists have used DOSS to track Corexit in the environment, DOSS does not always have a direct link to Corexit (see page 2). After the oil spill, the community of Orange Beach, Alabama, conducted its own water sampling to determine if DOSS was present in nearshore and inland waters. DOSS was found in the water samples, but it did not come from the dispersants used during DWH. The amount of DOSS in the samples was higher than expected given the samples' distance from where responders sprayed the dispersants. The more likely source of DOSS was from stormwater pollution from nearby communities, which use detergents, cosmetics, laxatives, and other everyday products that contain DOSS.[8]

Offshore waters

Another study found deep-sea coral communities covered in brown clumps of material containing oil from the well. The

Ships make their way through surface oil. (Daniel Beltra/Greenpeace photo)

Response crews battling the fires of the offshore oil rig. (USCG photo) corals were located 4,500 feet below the surface and up to seven miles from the wellhead. Scientists sampled the coral communities six months after the DWH oil spill and found DOSS was still present.[7] The breakdown of DOSS is slower in deeper waters where lower temperatures delay the uptake by bacteria[9] and sunlight cannot penetrate.[10]

Dispersants being released by plane. (NOAA photo)

EFFECTIVENESS

Both chemical and environmental factors determine how well dispersants break up oil. The type of oil, the amount of oil, how **weathered** the oil is, the type of dispersant, and how the dispersants are applied to the oil can influence how well dispersants work. Physical properties of the water, such as temperature, water **salinity**, and wave energy, may also affect the dispersants' effectiveness.[11] Dispersants are less effective on oils that have:

- Higher viscosity, the oil is thick and doesn't flow easily;
- Weathered causing the oil to become more viscous or have a thicker consistency;
- Cooled significantly below their pour point, which is the lowest temperature at which a liquid remains pourable, or;
- Emulsified, when two liquids such as oil and sea water combine and mix.[12]

SURFACE APPLICATION OF DISPERSANTS

During the DWH oil spill, responders applied chemical dispersants to the oil slick at the sea surface using planes and boats. This method exposed the dispersants to direct sunlight, which could have caused some of the ingredients in them to be less effective. To understand what happened to the dispersants in the environment, scientists tested four ingredients found in Corexit (2 butoxyethanol, dioctyl sodium sulfosuccinate (DOSS), dipropylene glycol butyl ether, and propylene glycol) to determine whether sunlight affected them. They discovered that the exposure to direct sunlight did not directly affect the dispersants. However, the sunlight altered other chemical components in the water, which caused the Corexit to degrade.[13,14]

Floating or submerged materials, such as sea sand, mangrove leaves, seaweed, and seagrass, also influence the effectiveness of dispersants. In lab studies, scientists tested the role of different natural materials on dispersant effectiveness. When small amounts of

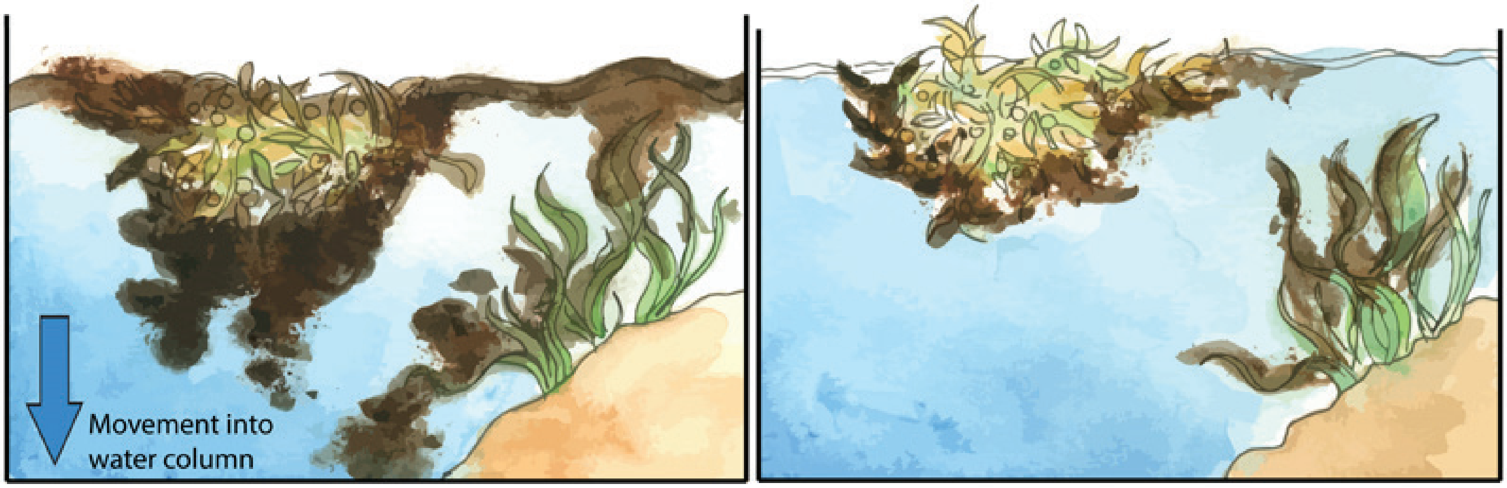


FIGURE 2. *The effect of partially submerged natural materials on the transfer of oil from the surface to the water column.* **LEFT:** *With large amounts of floating oil (shown in brown), the natural materials transfer the oil from the floating-oil layer to the water column making more oil available to be dispersed and broken down.* **RIGHT:** *With relatively small amounts of floating oil, the natural materials retain the oil, causing less oil in the water column, and reducing the effectiveness of the dispersant. (Florida Sea Grant/Anna Hinkeldey)*

floating oil were present, natural materials (such as seaweed) that float on the surface adsorbed the oil. The dispersant was less effective because there was less oil in the water column to disperse. However, when there was a large amount of floating oil, wave action moved the seaweed and similar materials causing the oil to be mixed into the water column. This made the dispersant more effective at breaking down the oil (Figure 2).[15]

DEEP-WATER APPLICATION OF DISPERSANTS

Before the DWH oil spill, responders had never used dispersants in deep water to break up oil. While responders were applying Corexit almost one mile below the sea surface, the federal government started a monitoring program to test the effectiveness of the dispersant. They also monitored how the dispersant was affecting the environment, water and air quality, and human health. Results from the program indicated that the dispersant was effective at breaking up oil and reducing the amount of oil that reached the surface. According to the U.S. Environmental Protection Agency (EPA), applying the dispersant at depth meant a smaller amount of dispersant was needed compared to what would be needed to disperse the same amount of oil once it reached the surface.[16] It also reduced the amount of oil reaching the ocean surface and minimized human contact with dispersants. The monitoring plan developed and used during the DWH oil spill is available on U.S. EPA's website and listed in the reference section.[17]

Some scientists have been unable to determine whether applying a dispersant at depth was successful in breaking down oil into smaller droplets (Figure 3).[2] Studies show that DOSS, and possibly other chemicals

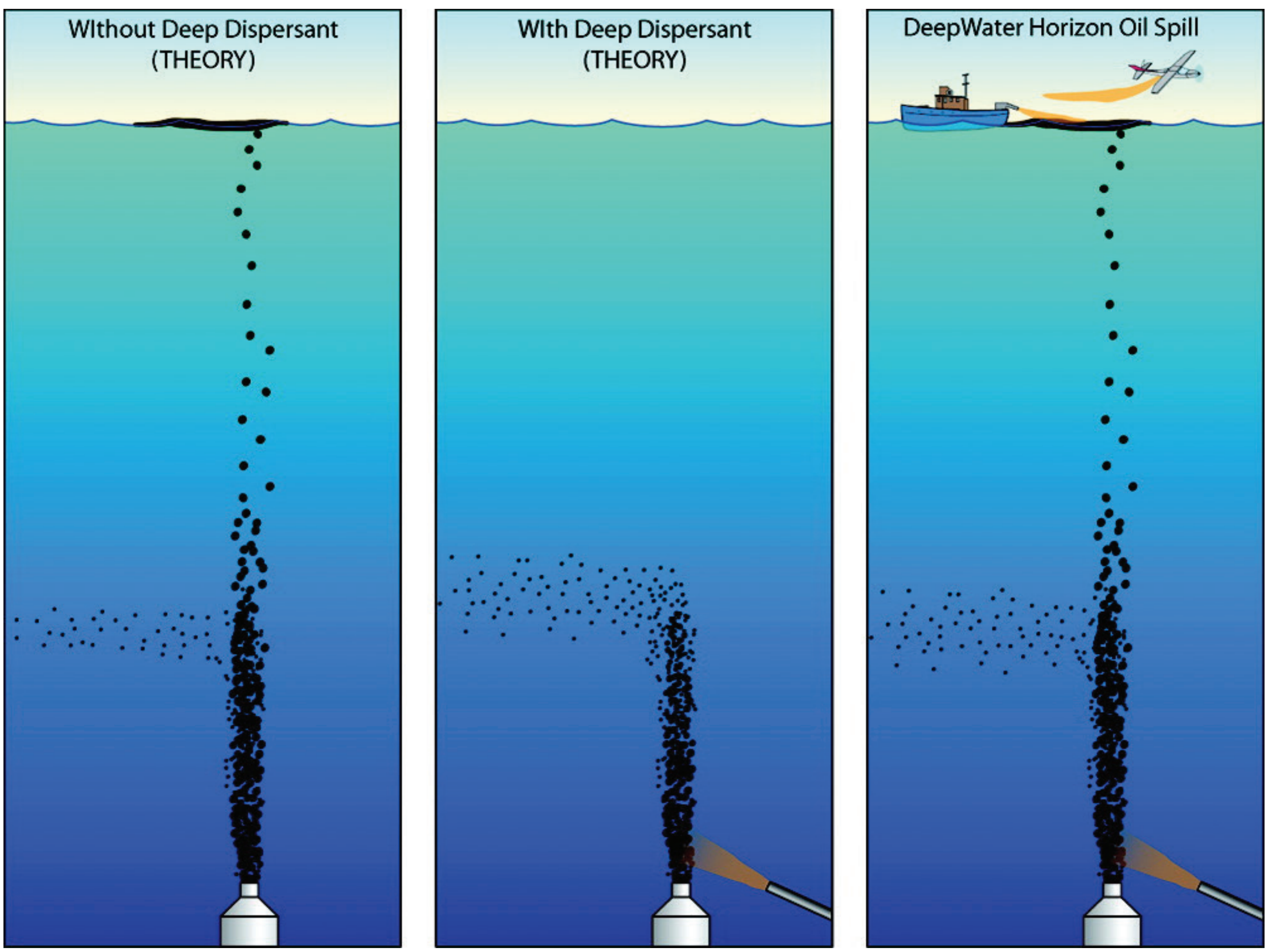


FIGURE 3. *Graphic showing the theoretical fate of the oil with and without subsurface dispersants and what occurred during the DWH oil spill. In theory, if no dispersants were applied at the wellhead, oil would have become trapped in an underwater plume and risen to the surface (left image). If dispersants were applied at the wellhead, oil would not rise to the surface but would become fully contained in an underwater plume (middle image). During the DWH oil spill, the oil behaved in both ways. Dispersants were applied at the surface and at the wellhead, some oil became trapped in an underwater plume and the rest rose to the surface (right image). (Kujawinski[1])*

found in Corexit, became trapped in the deep plumes. There were two competing explanations for this entrapment:

1. Dispersants were highly effective. Corexit was found in small oil droplets trapped in the plume. If DOSS was deposited in these small oil droplets, then it would suggest that the dispersant was highly effective and caused the oil to break up into small droplets.
2. Dispersants were not effective in the deep-water environment. DOSS dissolved into the water while it was rising from the wellhead, and through separation with water and natural gas, became trapped in the deep-water oil plume at roughly 3,600 feet. If DOSS dissolved, then the dispersant could not effectively disperse the oil.[2]

"Octopus" oil droplets are generated when oil premixed with dispersants is released in the water column. (Chang Li and David Murphy/DROPPS photo)

Other scientists do not agree that dispersant use below the surface was as effective. To test the effectiveness of dispersants, some scientists developed a **hydrodynamic model** that recreated the conditions during the DWH oil spill. The model indicated that the dispersants were not effective at depth and that applying them at the wellhead may not have changed the amount of oil rising to the surface. The model results suggested that the size of the oil particles being released at depth were already small and mostly neutrally buoyant, meaning they were not rising or were rising slowly. They were small and mostly neutrally buoyant because they were traveling through the wellhead at high speed and through a small diameter pipe.[18] Model results were confirmed in an experiment that used a **high-pressure visual autoclave** to evaluate the effect of droplet size on the movement of oil through the water column. Results indicated that using dispersants at depth only reduced the amount of oil reaching the sea surface by 1-3%.[19]

Do we need to be concerned with the effectiveness and persistence of dispersants in the Gulf of Mexico? Scientists learn more every day, but there are still many questions related to using a large amount of dispersants and applying them in deep waters. Future research from programs, such as the Gulf of Mexico Research Initiative (GoMRI), will continue to study the use of dispersants to determine their persistence and effects on the marine environment.

For more information about these ongoing studies, go to GoMRI's website:

http://gulfresearchinitiative.org

To learn more about how oil and dispersants impact aquatic life and how these organisms break down these chemicals, refer to our other publications which can be found on the Oil Spill Science Outreach Program website at: http://gulfseagrant.org/oilspilloutreach

GLOSSARY

Corexit 9527A and 9500A
Dispersants approved for use in US waters and those that were used to minimize the presence of surface oil slicks during the Deepwater Horizon oil spill.

Dioctyl sodium sulfosuccinate (DOSS)
A primary component of both dispersant formulas used in the Deepwater Horizon oil spill. It increases the attraction between oil and water molecules and hinders the formation of large oil slicks on the surface of the ocean. DOSS can also be found in consumer products such as detergents, cosmetics, and laxatives and, therefore, can be found in coastal waters.

Dispersants
Chemicals that are used during oil spill response efforts to break up oil slicks and can limit floating oil from impacting sensitive ecosystems such as coastal habitats.

Emulsify
Make into a fine dispersion of droplets of water and oil, with one being suspended in the other. For crude oils, it refers to the process where sea water droplets become suspended in the oil by mixing due to turbulence.

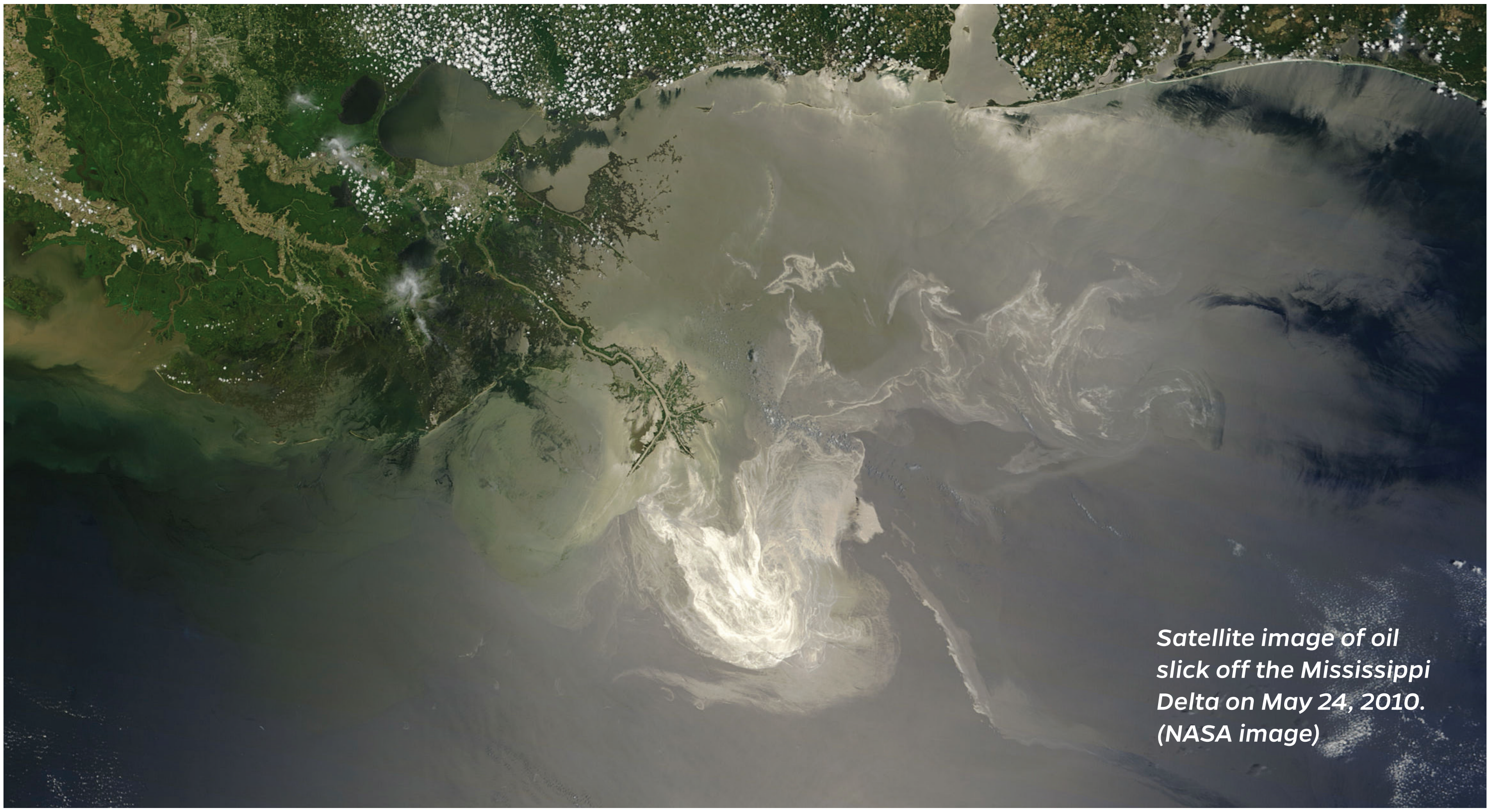
High-pressure visual autoclave
A device in which high pressure conditions can be established to measure the size of oil droplets in water.

Hydrodynamic model
Computer-based models used as a tool to describe the way a body of water moves.

Salinity
The average concentration of dissolved salts in a body of water.

Surfactant
Compounds that work to break up oil. Dispersants contain surfactants that break the oil slick into smaller droplets that can more easily mix into the water column.

Weathered oil
When processes such as evaporation, dissolution, bacterial decomposition, or exposure to sunlight change the chemical composition and physical appearance of oil.



Satellite image of oil slick off the Mississippi Delta on May 24, 2010. (NASA image)

REFERENCES

1. National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling. (2011). Deep Water The Gulf Oil Disaster and the Future of Offshore Drilling.
2. Kujawinski, E. B., Soule, M. C. K., Valentine, D. L., Boysen, A. K., Longnecker, K., & Redmond, M. C. (2011). Fate of dispersants associated with the Deepwater Horizon oil spill. Environmental Science & Technology, 45, 1298-1306.
3. Thibodeaux, L. J., Valsaraj, K. T., John, V. T., Papadopoulos, K. D., Pratt, L. R., & Pesika, N. S. (2011). Marine oil fate; knowledge gaps, basic research, and development needs; A perspective based on the Deepwater Horizon spill. Environmental Engineering Science, 28, 88-93.
4. National Research Council of the National Academies. (2005). Oil Spill Dispersants: Efficacy and Effects. Washington DC: The National Academies Press. Available: ***http://www.nap.edu/catalog.php?record_id=11283***.
5. Chapman, H., Purnell, K., Law, R., & Kirby, M. F. (2007). The use of chemical dispersants to combat oil spills at sea: A review of practice and research needs in Europe. Marine Pollution Bulletin, 54, 827-838.
6. National Center for Biotechnology Information. (2013). PubChem Substance Database; dioctyl sulfosuccinic acid compound summary, CID 23673837. ***http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=23673837***.
7. White, H. K., Lyons, S. L., Harrison, S. J., Findley, D. M., Liu, Y., & Kujawinski, E. B. (2014). Long-term persistence of dispersants following the Deepwater Horizon oil spill. Environmental Science & Technology Letters, 1, 295-299.
8. Hayworth, J. S., & Clement, T. P. (2012). Provenance of Corexit-related chemical constituents found in nearshore and inland Gulf Coast waters. Marine Pollution Bulletin, 64, 2005-2014.
9. Campo, P., Venosa, A. D., & Suidan, M. T. (2013). Biodegradability of Corexit 9500 and Dispersed South Louisiana Crude Oil at 5 and 25 °C. Environmental Science & Technology, 47, 1960-1967.
10. Batchu, S. R., Ramirez, C. E., & Gardinali, P. R. (2014). Stability of dioctyl sulfosuccinate (DOSS) towards hydrolysis and photodegradation under simulated solar conditions. Science of the Total Environment, 481, 260-265.
11. Fingas, M. (2011). Chapter 15 - Oil Spill Dispersants: A Technical Summary. In M. Fingas (Ed.), Oil Spill Science and Technology (pp. 435-582). Boston: Gulf Professional Publishing.
12. Coolbaugh, T., & McElroy, A. (2013). Dispersant Efficacy and Effectiveness. Available: ***http://crrc.unh.edu/sites/crrc.unh.edu/files/coolbaughmcelroy.pdf***
13. Kover, S. C., Rosario-Ortiz, F. L., & Linden, K. G. (2014). Photochemical fate of solvent constituents of Corexit oil dispersants. Water Research, 52, 101-111.
14. Glover, C. M., Mezyk, S. P., Linden, K. G., & Rosario-Ortiz, F. L. (2014). Photochemcial degradation of Corexit components in ocean water. Chemosphere, 111, 596-602.
15. Tansel, B., Lee, M., Berbakov, J., Tansel, D. Z., & Koklonis, U. (2014). Dispersion of Louisiana crude oil in salt water environment by Corexit 9500A in the presence of natural coastal materials. Estuarine, Coastal and Shelf Science, 143, 58-64.
16. United States Environmental Protection Agency. (2010). Questions and Answers on Dispersants. Retrieved from ***http://www.epa.gov/bpspill/dispersants-qanda.html***.
17. United States Environmental Protection Agency. (2010). Dispersant Monitoring and Assessment Directive for Subsurface ***Dispersant Application May 10, 2010***. Retrieved from ***http://www.epa.gov/bpspill/dispersants/subsurface-dispersant-directive-final.pdf***.
18. Paris, C. B., Henaff, M. L., Aman, Z. M., Subramaniam, A., Helgers, J., & Wang, D. P. (2012). Evolution of the Maconda well blowout: simulating the effects of the circulation and synthetic dispersants on the subsea oil transport. Environmental Science & Technology, 46, 13293-13302.
19. Aman, Z. M., Paris, C. B., May, E. F., Johns, M. L., Lindo-Atichati, D. (2015). High-pressure visual experimental studies of oil-in-water dispersion droplet size. Chemical Engineering Science, 127, 392-400.

SUGGESTED CITATION

Wilson, M., Graham, L., Hale, C., Maung-Douglass, E., Sempier, S., and Swann, L. (2015). Oil Spill Science: Persistence, Fate, and Effectiveness of Dispersants used during the Deepwater Horizon Oil Spill. GOMSG-G-15-004.

OIL SPILL SCIENCE OUTREACH TEAM

Christine Hale
Texas Sea Grant
chris.hale@tamu.edu

Larissa Graham
Mississippi-Alabama Sea Grant
larissa.graham@auburn.edu

Emily Maung-Douglass
Louisiana Sea Grant
edouglass@lsu.edu

Stephen Sempier
Mississippi-Alabama Sea Grant
stephen.sempier@usm.edu

LaDon Swann
Mississippi-Alabama Sea Grant
swanndl@auburn.edu

Monica Wilson
UF/IFAS Florida Sea Grant Extension
monicawilson447@ufl.edu

GULF OF MEXICO RESEARCH INITIATIVE

Sea Grant
Texas • Louisiana • Florida
Mississippi-Alabama

UF | IFAS Extension
UNIVERSITY of FLORIDA

NOAA
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
U.S. DEPARTMENT OF COMMERCE

This work was made possible in part by a grant from The Gulf of Mexico Research Initiative, and in part by the Sea Grant programs of Texas, Louisiana, Florida and Mississippi-Alabama. The statements, findings, conclusions and recommendations do not necessarily reflect the views of these organizations.

GOMSG-G-15-004