



OIL SPILL SCIENCE

SEA GRANT PROGRAMS OF THE GULF OF MEXICO

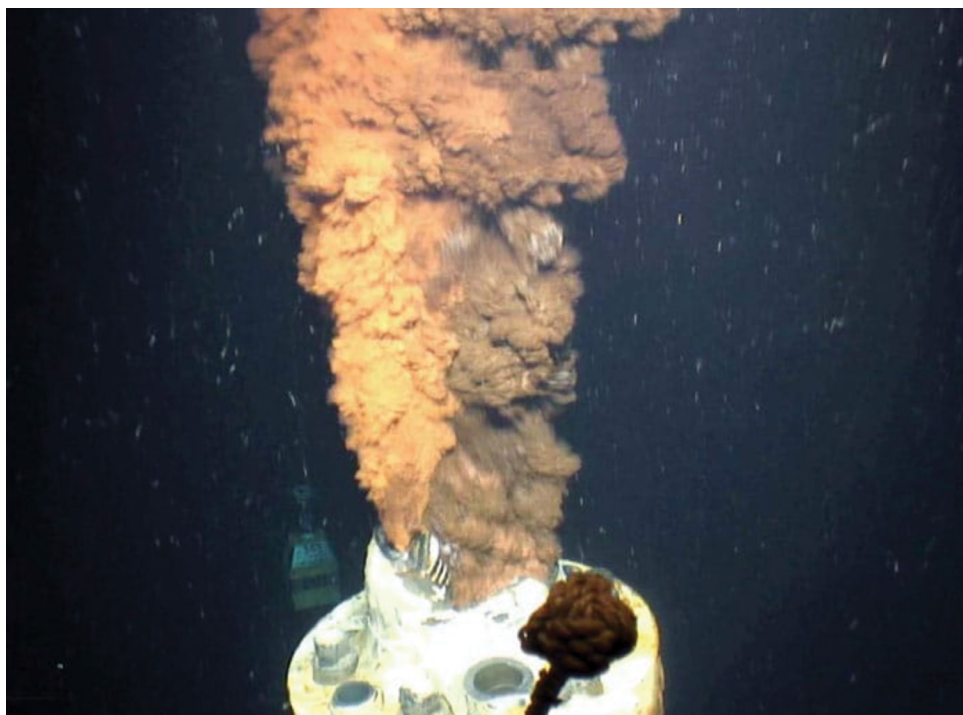
THE FATE OF OIL: INSIGHTS AFTER DEEPWATER HORIZON

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The years since the Deepwater Horizon oil spill have deepened society's scientific understanding of how oil breaks down and interacts with the environment at the chemical level.

Crude oil is produced over millions of years through the transformation of prehistoric marine life into a complex mixture of chemicals. Humans can extract the resulting mixture from the earth and refine it. The products created from refined crude oil are used to fuel our cars, heat our homes, and produce everyday items like plastic and petroleum jelly.

During activities such as extraction or transportation of crude oil, accidental spills sometimes occur in marine waters. Once released into the water, crude oil begins to age and break down, moving through the marine environment along various pathways.^{a,b} A variety of environmental factors—physical, chemical, biological— influence these changes, which are



SYNTHESIS SERIES

The purpose of this publication is to exclusively reflect findings from synthesis activities supported by the Gulf of Mexico Research Initiative (GoMRI). GoMRI synthesis documents are the primary references for this publication. The summary may also include peer-reviewed publications and other reports cited in the GoMRI synthesis activities that help to provide foundation for the topic.



collectively known as **weathering** processes (**Figure 1**).^a Though weathering processes are generally understood, the circumstances surrounding each oil spill are unique as every oil has a distinct chemical composition and the marine environment is ever-changing. These factors cause many gaps in our scientific knowledge of what happens to oil in the environment after a spill occurs.

One of the largest spills in history, the Deepwater Horizon (DWH) oil spill provided scientists an opportunity to better understand

The Deepwater Horizon oil spill occurred in April 2010 when the MC252 wellhead, located approximately 50 miles from the Louisiana coastline and one mile beneath the water's surface, released millions of gallons of crude oil and natural gas into the Gulf of Mexico. (U.S. Geological Survey)

the fate of the oil in the offshore deepwaters and coastal environment of the Gulf of Mexico. During the 2010 spill, a wellhead nearly one mile beneath the water's surface released nearly 134 million gallons of **crude oil** and gases into the waters of the Gulf of Mexico.¹ Portions of the crude oil rose from the deep, making its way to water's surface and forming oil slicks, posing a threat to marine life and nearby coastal habitats. In an effort to reduce the formation of oil slicks and enhance natural weathering processes, including those by microbes, emergency responders applied close to 1.8 million gallons of **dispersants**, both on the water's surface and directly at the wellhead deep underwater. Small amounts of oil dispersed at the wellhead became caught up in deep, underwater currents running parallel to the seafloor. Despite best efforts, some of the weathered oil from the water's

surface made its way to shore. Some of the weathered oil from both the water's surface and deep depths combined with particles in the water and sank to the seafloor.

DRIVING FORCES

What kinds of changes due to weathering did DWH oil experience during its journey through the environment? What were the driving forces behind those changes?

To understand the fate of the oil involved in the DWH spill, the chemical components of the crude oil involved must be considered. Crude oil consists mainly of **hydrocarbons**—compounds composed of hydrogen and carbon. Multiple types of hydrocarbons, each with their own unique chemical structures and properties, exist in crude oil.^{a,c} Prior to the DWH oil spill, scientists knew that **volatile** compounds in crude oil rapidly evaporate from the water's

surface in the hours after an oil spill. In fact, evaporation accounts for much of the initial loss of oil volume.^{a,d} However, scientists and responders had limited information about the speed and extent that other processes contribute to the fate of oil post-spill. They wanted additional insight into the role that sunlight, **microbes**, dispersants, and movement to the seafloor play in the fate of oil.

Breakdown with sunlight

In the 10 years of research since DWH, scientists have learned that the breakdown of oil by sunlight may contribute as much to oil weathering as evaporation does during the early weeks of an oil spill. Previously, it was thought that sunlight played a relatively minor role in oil weathering.^d However, scientists found that more than 60% of the breakdown of DWH oil by sunlight occurred in the surface waters

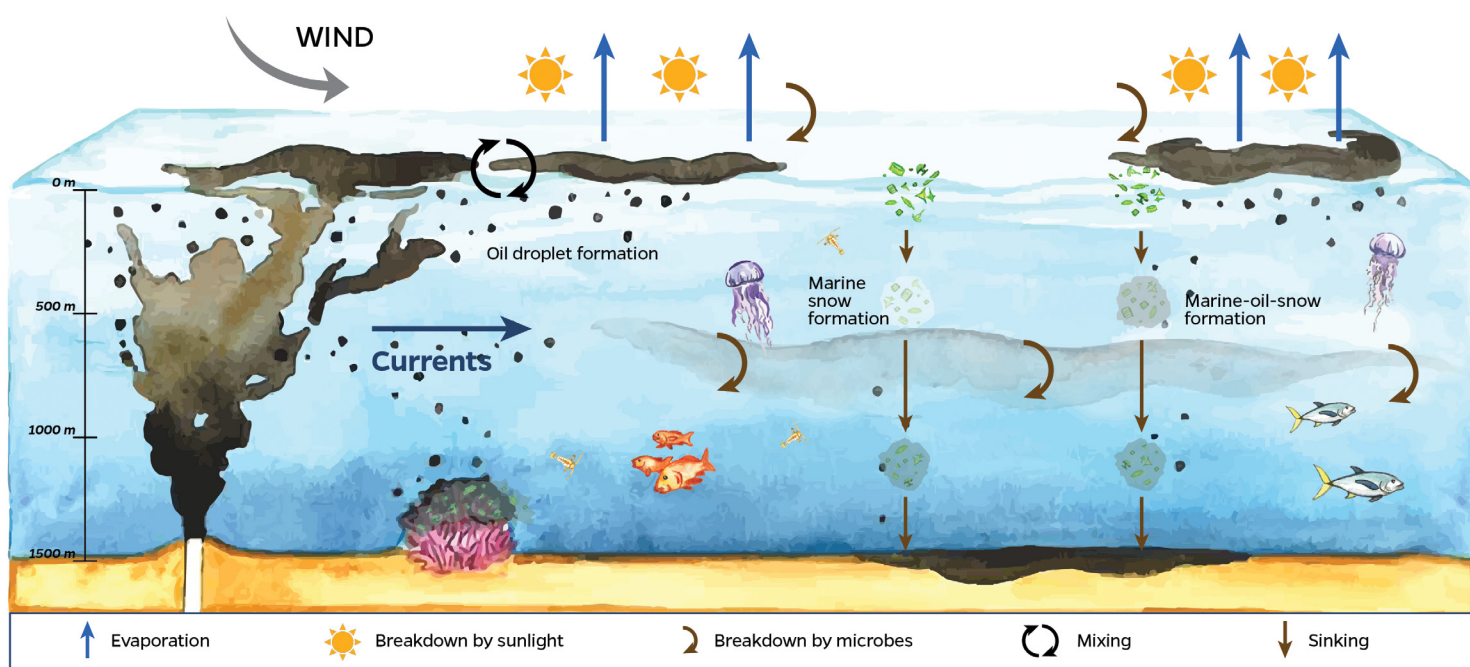


FIGURE 1 (not to scale). After the Deepwater Horizon oil spill, multiple weathering processes broke down the crude oil released from the wellhead located at the seafloor (far left). While some oil rose to the surface to form oil slicks, some oil droplets mixed in the water and were consumed by animals and microbes, incorporated into marine oil snow, sank to the seafloor, or caught in currents in deeper waters to form the deep intrusion layer. (Anna Hinkeldey, adapted from Passow & Overton, 2021)

within the first couple of weeks of the DWH spill.^{b,d}

Through a process called photooxidation, sunlight breaks down certain hydrocarbon compounds found in crude oil (**Figure 1**). Not all of the hydrocarbons in crude oil react directly with sunlight.^d However, scientists discovered that when sunlight reacts with the light-absorbing compounds in oil it can create oxygen-containing compounds.^d These oxygen-containing compounds then react with other compounds in oil not directly affected by sunlight, causing them to break down as well. This cascade-like effect allows for much more of the oil on the water's surface to react with and be broken down by sunlight than previously understood.

As sunlight weathers oil, it transforms into an **emulsion**—a thick, goey consistency that is not easily broken up by dispersants and may be difficult to clean up using other response measures such as burning.^d Further, while large, complex molecules called asphaltenes naturally occur in crude oil, more similar compounds may form as a result of reactions with sunlight and other weathering processes, and they are not easily broken down.^a

Breakdown by microbes

Microbes significantly contribute to the breakdown of oil in the months and years after an oil spill.^b Microbes are found throughout marine and coastal environments, in and on both the water and the **sediments** of beaches and wetlands. Some species of microbe already present in the Gulf of Mexico prior to the DWH spill had the ability to use compounds found in oil as a food source.^b Typically, oil-consuming

microbes are present only in small numbers, but they reproduce rapidly in the presence of oil, their food source. In fact, the communities of microbes present in the water and sediments along shore and on the seafloor shifted in favor of larger numbers of oil-consuming microbes post-DWH.^{b,e} Some microbes formed films that enveloped floating oil droplets and formed sticky webs of mucus, creating what scientists call **bacteria-oil agglomerations (BOAs)**. In some cases, microbes also released naturally-produced **surfactants** that aided the microbes in the breakdown of hydrocarbons.

Different species of microbe are uniquely suited to break down specific compounds that make up oil. The population levels of individual species of microbe rose and fell in succession, each species growing in abundance as it took its turn breaking down the type of oil compounds it was best equipped to consume. Generally speaking, smaller, simpler chemical structures were more easily broken down by microbes than larger or more chemically complex compounds or some compounds already chemically changed by sunlight.² Some of those oil compounds not easily broken down by microbes may remain in deep water, beach, and marsh sediments decades after a spill.^b

In addition to chemistry, weathering of oil by microbes is controlled by the amount of **nutrients** available. Low nutrient levels can stunt the ability of microbes to break down oil. For example, scientists found that low nutrient levels at the water's surface reduced microbes' ability to break down surface slicks despite their presence in the area.^b Similarly, oxygen is an important ingredient for

microbe activity.^b While oil breakdown can occur by microbes even in low- or no-oxygen environments, breakdown is enhanced by the presence of oxygen. In fact, oxygen is so important for the rapid breakdown of oil that scientists used oxygen levels to monitor hydrocarbon breakdown in the deep sea.^b

Dispersing the oil

The application of dispersants at the wellhead during the DWH oil spill caused some of the oil released to break into droplets in the deep sea. The larger oil droplets dispersed at the wellhead rose to the water's surface. There they joined together to form oil slicks hours after being released from the wellhead. Emergency responders applied additional dispersants on the water's surface to help break up the large oil slicks into small oil droplets and speed up further weathering by microbes in the water.^b

The tiniest of the oil droplets dispersed at the wellhead—less than the thickness of a human hair in size—along with gases and other types of oil compounds became caught up in and traveled with deep-sea currents running parallel to the seafloor. This movement of low concentration gases and oil droplets in the subsea formed what scientists now call the **deep intrusion layer (Figure 1)**.^c While concentrations of these of oil droplets and gases were low, levels were higher than typical in a marine environment. The deep intrusion layer formed in the waters approximately 3,600 feet beneath the surface. It was about 660 feet thick and spread over an area of 4,400 square miles.^{b,c} Microbes that formed BOAs around micro-droplets in the deep intrusion layer were able to appreciably break down some

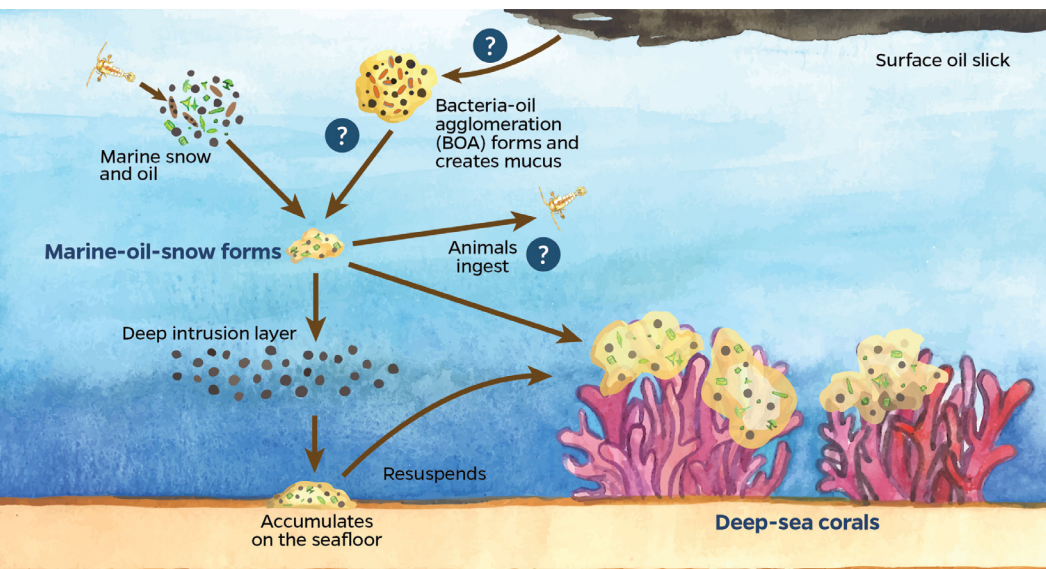


FIGURE 2 (not to scale). Scientists believe a complex group of interactions come together to form the marine oil snow that eventually sinks to the seafloor during marine oil snow sedimentation flocculent accumulation (MOSSFA) events. Microbes (in orange) can envelope and break down oil droplets in the water, forming a bacteria-oil agglomeration (BOA). This BOA releases a sticky mucus that may also combine with oil and marine snow, which can include phytoplankton (shown in green) and matter such as fecal pellets (brown ovals) which can contain oil (brown ovals with black dots). The mixture of oil and marine snow forms marine oil snow, which can collect additional oil in the deep intrusion layer, transport weathered oil to the seafloor, and blanket deep-sea corals and other seafloor-dwelling organisms. Question marks indicate linkages still under scientific investigation. (Anna Hinkeldey, adapted from Burd et al., 2020)

oil compounds in just over a week.^b Three groups of microbes played major roles in the deep intrusion layer—*Oceanospirillales*, *Colewellia*, and *Cycloclasticus*—breaking down roughly 60% of the oil compounds within just months after the start of the spill.^b Each group specialized in consuming different hydrocarbon types.

Research revealed that the dispersants applied at the water’s surface and at the wellhead modified some of the oil weathering processes.^{b,f} For example, dispersants improved the ability of oil and water to mix, which allowed smaller oil droplets to form than would be possible through natural

processes alone. While these tiny droplets were more readily broken down by microbes than oil slicks or larger droplets, dispersants may have also inhibited some oil-consuming microbes.^{b,f} Scientists also found dispersants can reduce the amount of surface oil lost to evaporation since more oil was mixed into the water mass below the surface.^{b,f}

Carrying oil to the seafloor

The delivery of weathered oil residues to the seafloor during DWH occurred via multiple pathways that all intersect.^{b,e} One route involved fine particles of sediment that stuck to oil droplets and sank. Scientists also found that BOAs enabled oil to

reach deeper water depths as well as entangle other matter, such as **phytoplankton**. Another pathway called **marine oil snow**, a mixture of marine snow and oil, has been the focus of much study (**Figure 2**). Marine snow refers to the collective mixture of sediment, fecal matter, BOA mucus, phytoplankton, and bits of decaying plants and animals that sink down to the seafloor from the upper layers of the water.^e Some of this sinking marine snow serves as the food source for marine animals.

If weathered oil droplets are present in the water, in fecal pellets, or stuck to sediment or mucus, they can combine with the marine snow, creating ‘marine oil snow.’ The application of dispersants during DWH may have stimulated some species of phytoplankton to produce large amounts of mucus, creating even more marine oil snow.^{b,e} Eventually, marine oil snow mixtures clump and sink to the seafloor in a process called sedimentation. This combination of clumping and sinking acts as a vehicle for weathered oil, carrying it to the seafloor where it can accumulate and be buried. Such an event is called Marine oil snow Sedimentation and Flocculent Accumulation (MOSSFA). MOSSFA events occurred as a result of the DWH oil spill.^e

MOSSFA accounted for roughly 20% of the oil not recovered by emergency responders at the wellhead.^{b,e}

Oil can have a wide range of impacts to the seafloor.^{b,e} The presence of weathered oil altered the mixture of the microbes living there, creating a shift in favor of species that break down oil.^e Additionally, the large amounts of MOSSFA from the spill were present on the seafloor in some areas. Deep-sea corals near the MC252 wellhead became stressed

by MOSSFA cover, resulting in portions of the coral dying and other portions being overtaken by other organisms.^e This blanket of MOSSFA also reduced the ability of soft-bodied, seafloor-dwelling organisms to dig and burrow—a process that would normally mix oxygen into the sediments and enhance oil breakdown.^b For these reasons,

MOSSFA rested on the seafloor in some areas near the wellhead for months to years after the spill. With normal routes to replenish oxygen hampered, the low oxygen levels resulted in less than 1% of the weathered DWH oil being broken down in the deep-sea sediments near the wellhead five months after arriving on the seafloor.^b

HOW IS THE SOURCE OF OIL COMPOUNDS DETECTED?

Hydrocarbons can enter the marine environment through oil spills and naturally occurring oil seeps. How do scientists know if oil originated from the DWH oil spill or another source? It starts with scientists taking samples from multiple types of environments—including water from the sea surface and deep sea, and sediments from the seafloor and shoreline. For example, water samples from shallow depths can be taken from the side of a ship, using a sampling device called a rosette (**Figure 3**). Scientists obtained samples from the deep sea using an autonomous underwater vehicle (AUV) called *Sentry*, fitted with a sophisticated, chemical analysis instrument (**Figure 4**). This major advancement in technology improved scientists' ability to monitor

locations, like the deep intrusion layer, for oil compounds without carting water samples back and forth to the surface.^a

During DWH, scientists were able confirm the source of oil compounds in the water samples as coming from the MC252 wellhead by analyzing biomarkers.⁹ Biomarkers are the compounds in oil that do not break down easily over time and are a kind of chemical fingerprint, unique to the oil's place of origin, and used to distinguish one source of oil from another. Looking for these concentrations of these relatively stable compounds in a sample, scientists could confidently identify DWH oil in water versus that from other sources and detect how weathered the oil was.

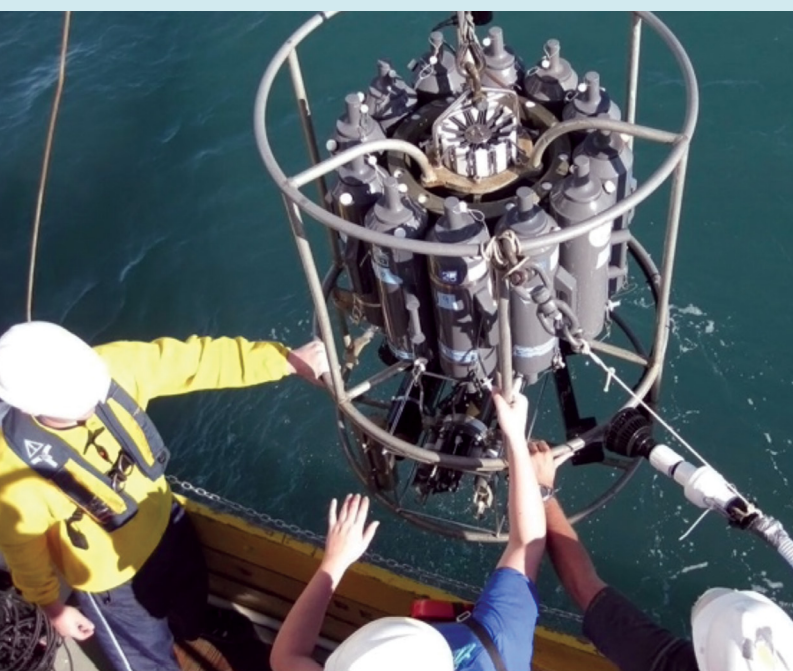


FIGURE 3. Sampling rosette. (Wei-Jen Huang)

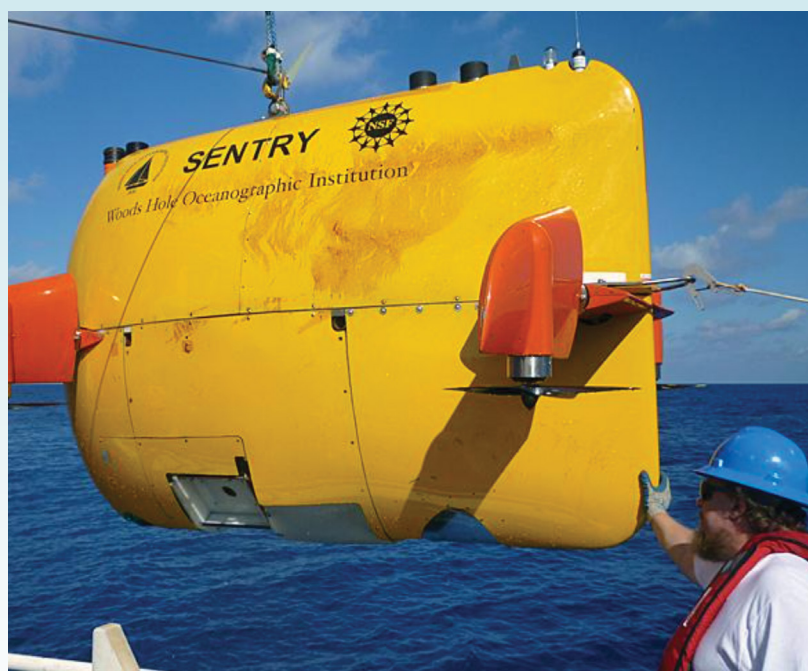


FIGURE 4. AUV *Sentry* (WHOI/Cameron McIntyre)

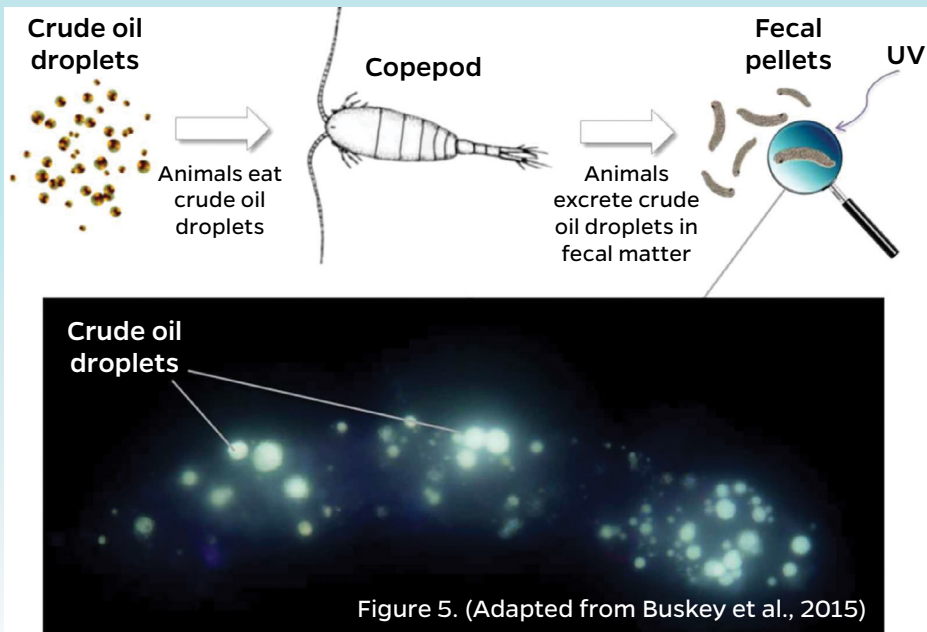


Figure 5. (Adapted from Buskey et al., 2015)

EXCRETING OIL TO THE SEAFLOOR

After an oil spill, crude oil droplets can be consumed by some marine life (**Figure 5**; top panel). In the lab, scientists used UV lights to detect the glow of crude oil droplets (**Figure 5**; bottom panel) in the fecal pellets of **copepods**.³ As these fecal pellets containing crude oil exit the animal, they may combine with other matter in the surrounding water such as phytoplankton, decaying bits of plant and animal matter, and mucus from bacteria to form marine oil snow.

OIL REACHING THE COASTLINE

Despite the best efforts of emergency responders, oil from the DWH spill impacted more than 1,100 miles of shoreline in the northern Gulf of Mexico. However, by the time the oil reached coastal beaches and wetlands, it was already chemically changed by weathering processes that occurred in the water, on the water's surface, and by the sun. Much of the floating oil emulsified into a mousse-like consistency.^a

Once on the tidal zone of beaches, the weathered oil mixed and clumped together with sand and shell, forming **sand-oil-aggregates (SOAs)** or sometimes called **sand and oil agglomerates**.^{a,b} Mats of SOAs often became buried in the sand through wave action. Broken bits of the mats occasionally made

their way to the beach surface as surface residual patties (between 4 inches and 3 feet) or smaller surface residual balls (less than 4 inches). The breakdown of oil compounds did not stop there. Sunlight and microbes continued to weather the oil once on land, though to a much lesser degree than when the oil was first exposed to weathering processes.^b Scientists found that the porous nature of sand combined with wave action along the beach stirred up the sand, allowing oxygen to deeply penetrate the beach and support the further breakdown of oil by microbes.^{a,b} Also, sand within the SOAs created space within the sand-oil-aggregate for oxygen to flow, stimulating microbes and resulting in a loss

of between 77 and 99% of certain oil compounds.^{a,b}

Weathered oil that entered wetlands became buried in sediments or formed mats on the sediment surface (**Figure 6**).^b Some impacted wetlands had hydrocarbon levels as much as 100,000 times over their pre-spill levels. In stark contrast to sandy beaches, wetlands are composed of fine-grain sediments that can be tightly packed together, leaving little space for oxygen to flow. This dynamic creates an environment where oxygen levels are low even at very shallow depths. Because of these low oxygen levels,

FIGURE 6. Weathered oil from the Deepwater Horizon oil spill made it way onto wetlands in southeastern Louisiana. In some areas, mats of highly weathered oil sat on the surface of the marsh (large image). In other areas, mats of highly weathered oil on the surface of the marsh prevented the further weathering of oil buried underneath it, keeping it in liquid form (inset images). (Coastal Waters Consortium)



the additional breakdown of buried oil by microbes was much slower in wetlands than in beaches despite the presence of oil-consuming microbes in both environments.^b While some level of breakdown does occur, as indicated by the loss of small-sized oil compounds, scientists expect that some of the oil compounds buried in marshes will take decades to break down.^b In the years since DWH oil spill, scientists observed that buried oil compounds can become distributed through-

out the upper layers of the marsh.^a This outcome is likely the result of mixing due to storms or the natural exchange of water carrying some oil compounds between sediments at multiple depths in the marsh. In wetland areas that had dieoffs of marsh grasses due to heavy oiling, mats of highly weathered oil prevented the regrowth of grasses.^a In some cases, highly weathered oil mats had small amounts of less weathered oil trapped beneath it. Because of the low oxygen conditions in the marsh,

the small amount of trapped oil remained relatively protected from weathering elements and was still in liquid form a decade after the spill.

WHERE DO WE GO FROM HERE?

To learn more, visit the GoMRI website at www.gulfresearchinitiative.org. Visit the Gulf Sea Grant program website at <http://gulfseagrant.org/oilspilloutreach> to view other publications, about dispersants, sorbents, oil, and other topics.

GLOSSARY

Bacteria-oil agglomerations (BOAs) — Microbe-formed films that envelope floating oil droplets and produce webs of mucus.

Copepod — An invertebrate, lacking compound eyes or a carapace (shell) and usually having six pairs of legs on the thorax. These animals are crustaceans, distantly related to crabs and shrimp, and of the order *Copepoda*.

Crude oil — Naturally occurring, unrefined oil. Crude oil is refined to produce a wide array of petroleum products, such as heating oils, gasoline, diesel, lubricants, road asphalt, and gases such as propane and butane.

Deep intrusion layer — The subsea plume of carbon and hydrogen-based (hydrocarbon) gases and tiny oil droplets that formed 3,600 feet beneath the water's surface after the Deepwater Horizon oil spill.

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

Emuls(-ify, -ified, -ion) — Occurs when water and oil combine, 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.

Hydrocarbons — Compounds composed of hydrogen and carbon compounds.

Marine oil snow — The collective mixture of oil and marine snow (a mix of sediment, fecal matter, mucus released from microbes, phytoplankton, and bits of

decaying plants and animals).

Microbes — Microscopic, single-celled, living organisms that include bacteria (for example, Cyanobacteria, Proteobacteria, Actinobacteria) and fungi.

Nutrients — Natural compounds necessary for the growth of organisms, such as microbes and algae. They include but are not limited to nitrogen, phosphorous, and iron.

Phytoplankton — Microscopic algae that drift or float in bodies of water.

Sand and oil agglomerates/Sand-oil-aggregates (SOAs) — A term that refers to sand and shell pieces loosely bound by oil and can include oil mats, surface residual balls, and surface residual patties, as this term does not distinguish them by size.

Sediments — Natural materials (including rocks, minerals, and remains of plants and animals) broken down from rocks by weathering and erosion.

Surfactants — 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.

Volatile — Easily evaporated at normal temperatures.

Weathering — Process by which oil changes physically and chemically. Includes processes such as oil spreading, evaporation, dispersing, dissolving, settling on the seafloor, and breakdown by sunlight and microbes. These processes are influenced by factors (such as type of oil being weathered, temperature, waves, and bacteria present).

REFERENCES

Publications resulting from the GoMRI-supported synthesis activities serve as the primary references for this work. Additional supporting literature, either cited in GoMRI synthesis papers or necessary for foundational information about the subject, is also included.

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ABOUT THE GoMRI/SEA GRANT SYNTHESIS SERIES

The GoMRI Research Board established Synthesis & Legacy committees to review 10 years of oil spill science findings. Look for Sea Grant extension publications on these GoMRI synthesis topics:

- Observing and modeling oil plumes and circulation
- Combined ecosystem modeling
- Combined oil spill modeling
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- Microbiology, genetics, and oil spills
- Dispersant-related impacts from oil spill response

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