Geochemistry

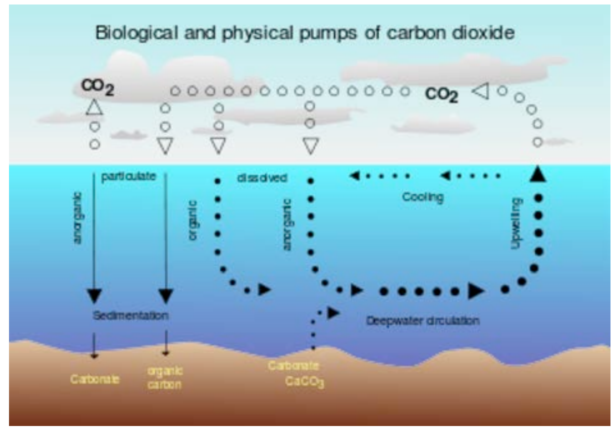
In the Gulf of Mexico

What is Geochemistry?

The study of the geological processes that affect the chemistry of the ocean.

Geochemistry in the Gulf

The Gulf of Mexico has many features that make it unique – from its natural oil seep ecosystems to asphalt extrusions. It is also considered a marginal sea because of borders that extend from the Yucatan Peninsula to encompass much of the southeastern United States. In addition, the Mississippi River, which drains approximately one-third of the contiguous U.S., transports about one million cubic yards of sediment, water, and nutrients per day to the Gulf. All of this contributes to the chemical composition of the Gulf of Mexico.



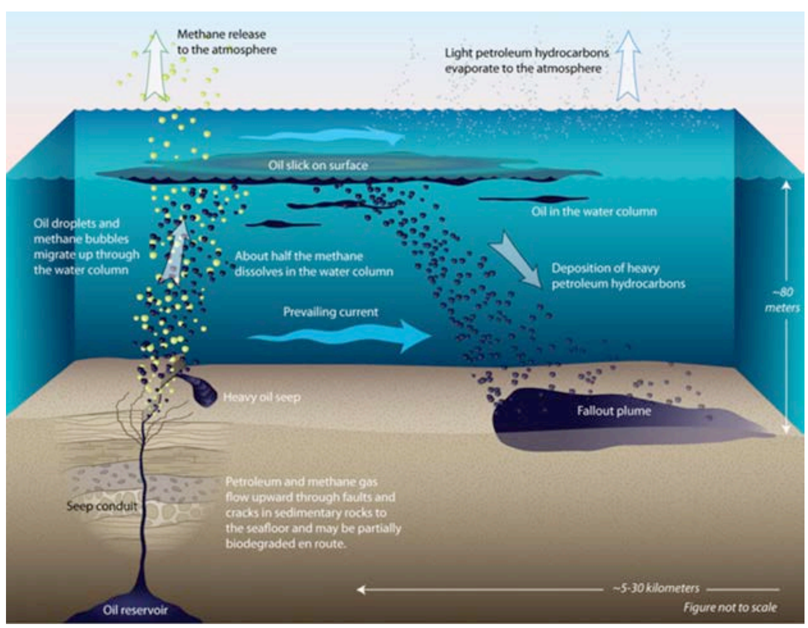
The biological pump acts as a filtering system for the ocean waters. Source: wikimedia

A process called the biological pump helps to regulate the movement of minerals and chemical elements as well as sediments and nutrients from the atmosphere and the surface of the ocean to the deep sea. The introduction of 4.9 million barrels of oil into the Gulf of Mexico during the 2010 Deepwater Horizon oil spill caused chemical oceanographers to wonder how the chemicals present in oil would be incorporated into the ecosystem and how would they degrade and weather over time.

Tracing the journey of hydrocarbons from the seafloor to the sandy beaches

Deep-C's geochemistry team was tasked with assessing the influence of oil and gas on water column and sediment biogeochemical processes and determing how this would affect biological productivity in the northeastern Gulf of Mexico. Researchers also investigated how hydrocarbons evolve under a variety of environmental conditions.

Evidence suggests that the fate of volatile compounds that either occur naturally in the sea (such as methane) or reach the sea through anthropogenic-induced pathways (such as mercury) was dramatically affected by the Deepwater Horizon oil spill. Understanding the impact of oil on the distribution and abundance of methane and mercury in the water column and in sediments, as well as its impact on primary production in the northeastern Gulf of Mexico, will help to answer the question *"what are the consequences for living organisms in the sea and on land?"*



This illustration shows the route traveled by oil leaving the sub seafloor reservoir as it travels through the water column to the surface and ultimately sinks and falls out in a plume shape onto the seafloor where it remains in the sediment. (Illustration by Jack Cook, WHOI) http://www.whoi.edu/oil/natural-oil-seeps

Deep-C Consortium Geochemical Research

Oil mixed with sediments to form marine oil snow

As plants and animals near the surface of the ocean die and start to decay, they slowly sink to the bottom of the seafloor. The transport of these types of particulates through the water column is called “marine snow” because the organic matter resembles flakes of snow as it falls. Researchers theorize that oil from the Deepwater Horizon spill mixed with marine snow and sunk at an accelerated rate due to flocculation, the process by which particles clump together and increase in mass. This may have led to dramatic increases in sediment accumulation rates on the deep sea floor. Deep-C researchers collaborated with scientists from all over the world to study the pathway that oil took from the surface to the seafloor. And why is this important? Dr. Uta Passow from the University of California-Santa Barbara summarized the need for this research. “The impact of the oil on the open ocean ecosystem when it is disbursed and diluted at the top of the water column is very different from the impacts it has when it sinks and accumulates on the seafloor. We need to know where the oil is to learn how to keep the damage to a minimum for the whole ecosystem, and for that we need to understand all of the pathways involved.”

New technology used to study oil weathering and degradation

A process called “gas chromatography” is typically used to separate oil into the individual elements that make up hydrocarbons. Next generation chromatography (performed at Woods Hole Oceanographic Institution) combined with ultrahigh resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry (a process used at the National High Magnetic Field Laboratory at FSU), can identify the tens of thousands of components in oil samples from the damaged well, tar balls collected along from along the Gulf Coast beaches, and contaminated beach sediments. This research is helping scientists improve our understanding of the degradation pathways for oil/hydrocarbons.

Gas chromatography: A carrier gas, such as helium or nitrogen is used to help separate chemical compounds.

An example of an oiled sand patty collected at Fort Pickens near Pensacola, Florida.

By tracing how oil weathers in the environment and breaks down over time, researchers gained invaluable insight into the physical and chemical processes that occurred between release and deposition. Between 2010 and 2014, researchers collected and analyzed more than 700 oiled sand patties along beaches from Louisiana to Pensacola, Florida. These samples were added to an online repository that will be used by scientists for years to come.

Methane in the water column

It is estimated that approximately a third of the hydrocarbon compounds released during the Deepwater Horizon oil spill was methane (CH_4). Methane occurs naturally in the deep sea and there is a robust ecosystem of methanotrophs that consume methane. During the oil spill, large plumes of methane were observed. After a few months, the plumes disappeared leading to a debate about their fate. This identified a need to study the rate of consumption and transport of methane when it enters the water column. Deep-C researcher Dr. Jeff Chanton (FSU) and colleagues used a process called “atomic forensics” to trace the origins of the methane in the water column. When plants turn sunlight into energy, the new carbon atoms carry a chemical signal – sometimes called "new carbon" – that fades away over thousands of years, after which it becomes "old carbon." Oil and gases like methane are millions of years old and thus made of purely old carbon. If plankton ate methanotrophs from the plume during the oil spill, those plankton should have more old carbon than run-of-the-mill Gulf of Mexico plankton, which typically eat food loaded with new carbon. In light of this research, it is believed that methane-derived carbon from the oil spill entered the food web via methanotrophy.

FSU PhD student Nick Myers collects water samples from the CTD (connectivity, temperature, depth) during a research cruise to analyze for the presence of methane (CH_4).

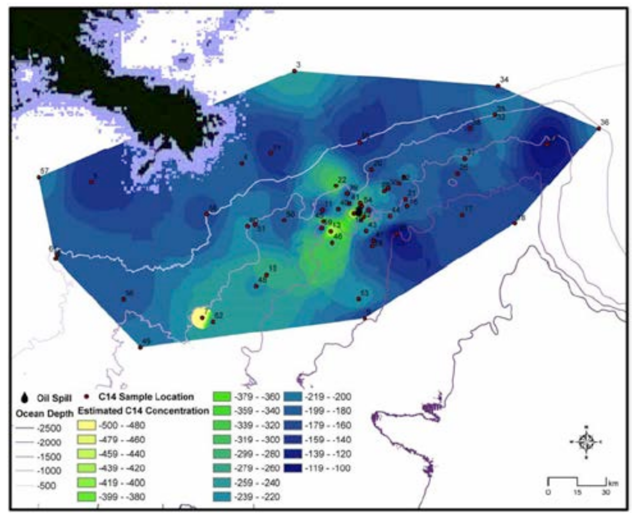
Bioaccumulation: Oil spill led to increased levels of MeHG concentration

Methylmercury (MeHg), the more toxic form of mercury, bioaccumulates through the food chain from the microscopic phytoplankton to the top predators such as sharks. Because it is an element, mercury does not break down into less toxic substances. In other words, as long as fish continue to be exposed to mercury, mercury continually builds up in their bodies and fish that eat other fish become even more highly contaminated. Thus, the largest tend to be the most contaminated. How does this relate to the Deepwater Horizon oil spill? Sulfate reducing bacteria are the primary producers of methylmercury, and the pulse of organic material from the oil spill resulted in a more oxygen-depleted environment where sulfate reducers can thrive. An analysis of several species in the northeastern Gulf of Mexico food chain conducted by FSU PhD student Alex Harper showed an increase in MeHg concentration following the spill which provides some evidence of the oil spill's marked effect on MeHg bioaccumulation in the food chain.

Sediment profiling for carbon 14

A cross section of a sediment core from the seafloor.

Researchers are using carbon 14, a radioactive isotope as an inverse tracer, to determine where oil might have settled on the seafloor. Unlike other sediments on the seafloor, oil does not contain carbon 14 so sediment that contained oil would immediately stand out in comparison. This process has allowed scientist to make predictions and draw conclusions about the amount of oil that is currently buried in the sediment of the seafloor. In collaboration with the Department of Geography at FSU, GIS mapping was used to create a map of the oiled sediment distribution on the sea floor (see image at right). Since less oxygen exists on the sea floor relative to the water column, the oiled particles are more likely to become hypoxic, meaning they experience less oxygen. When that happens, it becomes much more difficult for bacteria to attack the oil and cause it to decompose, leaving the oil in sediment to degrade very slowly.



Distribution of oil in the sediment near the site of the Deepwater Horizon oil spill.

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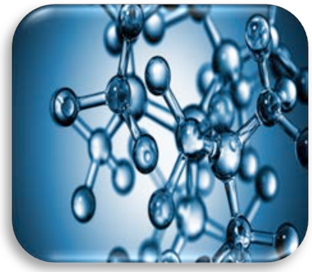
What Did We Learn?

- Following the Deepwater Horizon accident, released oil mixed with suspended particulate matter to form marine snow, which may have been deposited on the seafloor at an accelerated rate due to a process called "flocculation."
- Using a radioactive isotope called carbon 14, scientists were able to determine where oil was located in the seafloor sediment and a GIS map helped track its distribution.
- The oil spill increased the rate of bioaccumulation of methylmercury in some northeastern Gulf fish species.
- Methanotrophs consumed a large portion of the methane released by the Deepwater Horizon spill and this allowed methane from the oil spill to enter the food web.
- Innovations in next generation gas chromatography and FT-ICR Mass Spectrometry led to increased ability to fingerprint oil from its source and provided insight into the degradation of the biomarkers present in oil over time.
- Data collected led to an improved understanding of how oil breaks down in the environment and its effect on the biological pump that helps regulate the ocean's chemistry.

LESSON PLAN:
Chemical Components of the Gulf



Investigating the chemical processes of the ocean

Objective: To understand the composition of seawater, chemical processes which regulate the ocean and investigate factors that impact ocean salinity and chemical processes that regulate the ocean.

Standards: OLP 1, 4, 6; SC.912.E.7.1, SC.912.L.17.10

Time Required: One 50-minute class period

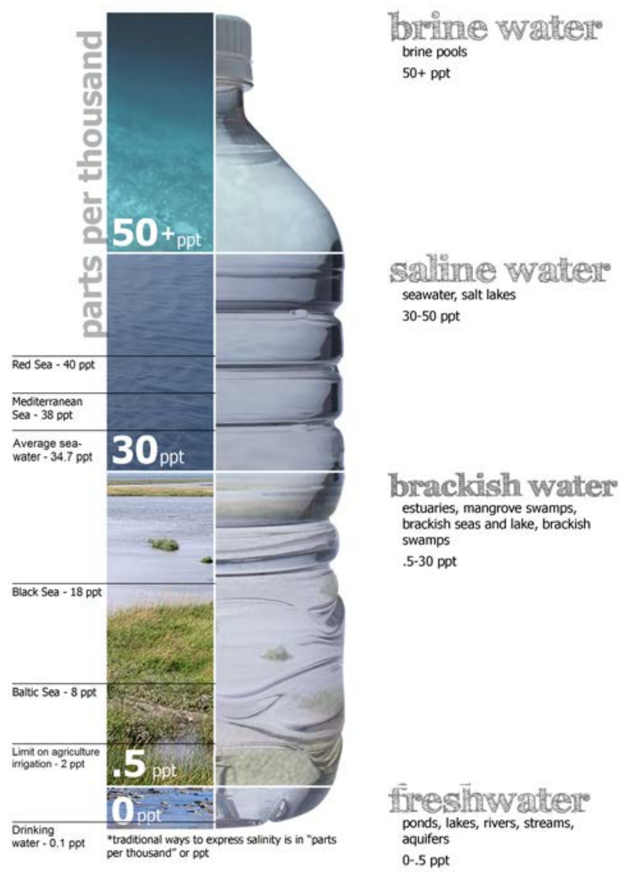
Keywords: biogeochemical cycles, chemical processes, salinity, upwelling, ppt (parts per thousand)

Materials:

- Graph paper
- Colored pencils
- Computer
- Hydrometer
- 500ml beaker of saltwater
- 500ml beaker of freshwater

Background

Did you know that almost all of the elements represented in the Periodic Table are present in the ocean? Chemicals in the ocean are part of an Earth system that recycles materials infinitely and the ocean is in delicate balance because of this. The Earth's systems contain fixed amounts of each stable chemical element and each element moves among reservoirs in the solid earth, oceans, atmosphere, and living organisms as part of **biogeochemical cycles** (i.e. nitrogen, water, carbon, oxygen, and phosphorus). An influx of chemicals from extreme weather events, increased industrialization, and environmental disasters such as the 2010 Deepwater Horizon oil spill can have a profound affect on the **chemical processes** in the ocean.



Source: http://commons.wikimedia.org/wiki/File:Water_salinity_diagram.png

Chemical oceanographers and marine chemists study the composition of seawater, as well as the interactions between the sun's energy, atmospheric compounds, dissolved and suspended oceanic organic and inorganic material, sea life, and the seafloor. Seawater is a mixture of water, salts, smaller amounts of other substances and atmospheric gases such as nitrogen, oxygen, and carbon dioxide. The six most abundant ions of seawater are chloride (Cl^-), sodium (Na^+), sulfate ($SO^{2}{}_{4}{}^{-}$), magnesium (Mg^{2+}), calcium (Ca^{2+}), and potassium (K^+). By weight, these ions make up approximately 99% of all sea salts. The amount of these salts in seawater varies around the world, due to precipitation and evaporation. Salt content is indicated by **salinity**, the amount of salt in grams dissolved in one kilogram of seawater and expressed in **parts per thousand** (ppt or ‰). That is, a salinity of 35‰ means 35 grams of salt per liter of seawater. The Northern Gulf has an average salinity of 36.2‰.

The salinity of the ocean can be affected by a variety of factors from the inflow of river water to **upwelling** that causes mixing of seawater. The introduction of nearly 5 million barrels of oil into the Gulf of Mexico's chemical cycle is bound to have an effect on the composition of seawater. Scientists studying the effects of the 2010 Deepwater Horizon oil spill on **chemical processes** of the ocean are investigating how oil breaks down over time, how it reacted with other chemicals, and pathways into the food chain. In this lesson, students will investigate the factors that impact ocean salinity, how components present in oil interact with other ocean chemicals, and gain an understanding of chemical processes that regulate the ocean.

Procedure

1. **Watch:** Have students watch the following Ted Ed video on Biogeochemical Cycles and answer the corresponding multiple-choice questions. http://ed.ted.com/on/mireRMZO.

2. **Measuring salinity**: (Prior to class prepare a beaker with saltwater and a beaker with freshwater. Set aside with hydrometer.) In this activity students will look at a specific ocean chemical – salt – and how its presence is influenced by environmental factors.

Major dissolved constituents in seawater with a chlorinity of 19 ‰ and a salinity of 34.32 ‰.			
Dissolved substance	Ion or compound	Concentration (grams per kilogram)	Percent by weight
Chloride	Cl^-	18.980	55.04
Sodium	Na^+	[illegible]	30.61
Sulfate	SO_4^{2-}	[illegible]	7.68
Magnesium	Mg^{2+}	1.272	3.69
Calcium	[illegible]	0.400	1.16
Potassium	K^+	0.380	1.10
Bicarbonate	HCO_3^-	0.14	0.41
Bromide	Br^-	0.065	0.19
Boric Acid	H_3BO_3	0.026	0.07
Strontium	Sr^{2+}	0.013	0.04
Fluoride	F^-	0.001	0.0
Totals		34.482	99.99

Discuss with students the chemical definition of salt and its presence in the ocean. Have students answer the following questions:

- Where do the salts come from?
- How do they get to the ocean?
- What processes increase salinity?
- What processes decrease salinity?
- How would the weather conditions this past spring affect salinity?
- Seawater has a fairly constant salinity; why might this be?

Explain to students that salinity is measured in ppt (parts per thousand). Demonstrate this by using the hydrometer to test the salinity of the prepared seawater and freshwater. How might the influx of fresh water affect the salinity of the salt water? Combine the freshwater with the salt water and test the salinity. Show students the table above that breaks down the major dissolved constituents in seawater.

3. **Factors that impact the salinity of the ocean:** Explain to the class that they will be comparing the salinity of two different locations. Pass out the graph paper and colored pencils. Using the table below, have the class plot salinity vs depth using the salinity values in column two using the red pencil. Put the salinity units on the x-axis across the top and depth on the y-axis, increasing from top to bottom. Using the blue pencil repeat this step using the data from column 3.

Have students answer the following questions:

- Describe the distribution of salinity with increasing depth.
- What might be causing the variations at the surface?
- Why is the salinity constant at depth?
- What is the difference between the two plots?
- What process is responsible for the salinity values in the surface water?

Depth (meters)	Salinity - #1 (parts per thousand)	Salinity - #2 (parts per thousand)
0	37.2	10.5
20	36.8	20.5
50	35.9	32.5
100	34.9	33.8
200	34.8	34.9
500	34.5	35.2
1000	34.9	34.9

4. **Literature Review:** Divide students into groups of 3-4 and assign them an element that is abundant in the ocean to research (i.e. methane, mercury, dissolved oxygen, carbon, sodium, etc.) and ask them to create a power point presentation to share with the class. Presentations should be 10 minutes long, consist of at least 10 slides, one video, and include the following information:
   - The source and structure of the element.
   - How the element reacts with other chemicals present in the ocean.
   - Toxicity of the element.
   - Human impact on the elements abundance and distribution.

Questions

1. Describe how biogeochemical cycles affect ocean processes.
2. What is seawater made up of? *Sodium, chlorine, other chemicals, metals, and minerals.*
3. What is salinity and how is it measured? *The amount of salt in grams dissolved in one kilogram of seawater*
4. What processes would increase or decrease salinity of the ocean? *Evaporation, influx of fresh water, temperature.*
5. How do humans impact the abundance and distribution of elements in the ocean? *Answers will vary.*
6. How do you think the oil spill influenced the chemical components in the Gulf of Mexico? *Answers will vary.*

Extensions

Pair this lesson with “Oceanography Demos” in the Physical Oceanography module (see page 91) to discuss how salinity affects density.

Conduct a desalinization lab.

Resources & References

Chemistry of the Gulf of Mexico
http://www.sarasota.wateratlas.usf.edu/upload/documents/Chemistry-in-GOM.pdf

More Salinity Activities
http://www.usc.edu/org/cosee-west/oceanglobe/pdf/densitysalinity/densityentire.pdf

National Ocean Service: Salty Questions
http://oceanservice.noaa.gov/facts/whysalty.html and http://oceanservice.noaa.gov/facts/riversnotsalty.html

“Parts Per Thousand” Lab from COSEE
http://www.ucar.edu/learn/1_4_2_14s.htm

Uncovering the Ocean’s biological pump
http://www.whoi.edu/oceanus/viewArticle.do?id=192409

“Why is the Ocean Salty?” By the U.S. Geological Survey
http://www.palomar.edu/oceanography/salty_ocean.htm

LESSON PLAN: Methane Mania

Investigating the influx of methane into the Gulf of Mexico food web

Note: This lesson plan works best in conjunction with the *Chemical Components of the Gulf* lesson.

Objective: To introduce students to the carbon cycle and its influence on the marine food web.

Standards: OLP 2, 5; SC.912.L.17.9, SC.912.L.17.10, SC.912.E.7.1

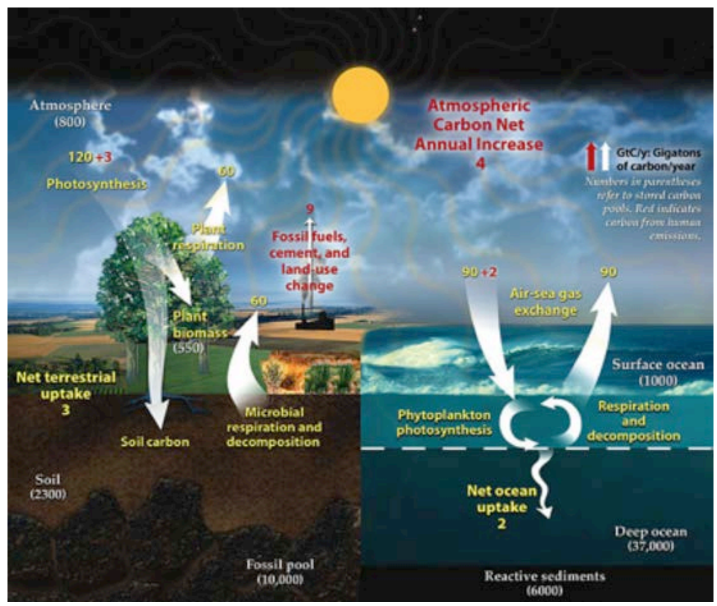
Time Required: At least two 50-minute class periods

Keywords: carbon cycle, methane, methanotrophy, marine food web

Materials: Computer and copies of the article, "*Study Confirms Methane-Eating Bacteria Contributed to Carbon Entering Food Web*" (see page 47)

Background

The **carbon cycle** is a biogeochemical process that is one of the keys to life on Earth. Carbon is one of the main components of all biological entities and as such is constantly being recycled and is in a delicate balance. There are many activities that can cause a disruption in the carbon cycle including geothermal events such as volcanoes and seeps as well as those caused by the action of humans such as the 2010 Deepwater Horizon oil spill in the northern Gulf of Mexico. Scientists and concerned citizen scientists are wondering what the effect of the oil spill has been on the carbon cycle and therefore the **food web** that is intricately connected with the flow of carbon in the ocean.



The Carbon Cycle in action
http://en.wikipedia.org/wiki/Carbon_cycle#/media/File:Carbon_cycle.jpg

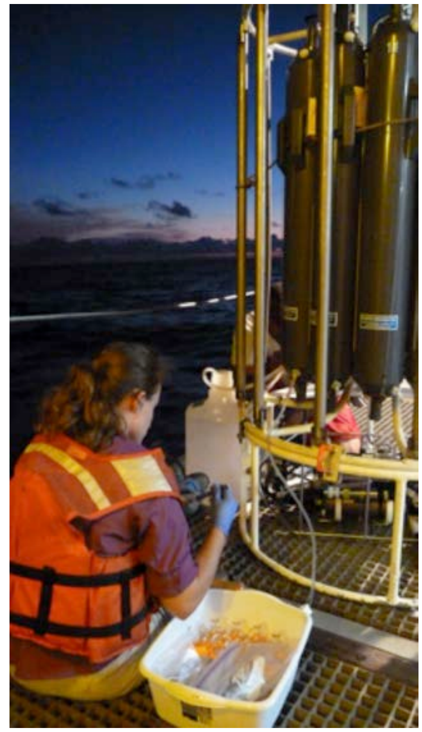
Researchers from FSU and their collaborators throughout the southeast have discovered a pathway for **methane** (CH_4), a colorless, odorless and combustible gas that was released along with the crude oil from the spill. Specialized bacteria called **methanotrophs**, consumed the methane that was released and transferred it up the food chain through the zooplankton that ate the bacteria. The abundance of methane caused a bloom of microbes to feast on the released gas. These methanotrophs helped to mitigate the effects of the spill and demonstrate the resiliency of the ocean's cycles. Understanding the carbon cycle and its influence on marine food webs is essential to determining the potential affects of an influx of methane into the Gulf of Mexico ecosystems. In this lesson students will gain an understanding of the carbon cycle, its influence on the food web, and the potential pathways for methane to have entered the marine food web in the Gulf of Mexico.

Procedure

1. **Demonstration:** Discuss the carbon cycle with students. Conduct a "Methane Mamba" experiment like the one here: http://chemmovies.unl.edu/chemistry/beckerdemos/BD015.html or watch a video like the one here: http://www.stevespanglerscience.com/lab/experiments/methane-mamba-tower-of-bubbles to show students how methane, a key component of the carbon cycle and a byproduct of the oil spill, behaves.

2. Research: Have students research the carbon cycle and write a two-page report on the different stages and the role of methane in the carbon cycle. Require two graphics and cited sources from either academic or government sources.

3. Group Project: Divide students into groups of two or three. Have students' research and create a multimedia presentation that accurately depicts the marine food web in the Gulf of Mexico and explains a potential pathway of the methane from the oil spill into the food web. This should be done as a multi-day assignment.



FSU graduate student Kelsey Rogers takes water samples that will later be analyzed from the presence of methane and other chemical components.

4. Evaluation: To test their theories on pathways for methane to enter the marine food web, have students watch the video "Food Web" from FSU researchers Ian MacDonald and Jeff Chanton. https://ecogig.org/content/ecogig-food-web and read the article, "Study Confirms Methane-Eating Bacteria Contributed to Carbon Entering Food Web" and answer the following questions:

- Approximately what percentage of the carbon-composing plankton collected in 2010 and 2011 could be attributed to carbon released by the oil spill?
- How were researchers able to match the carbon found in plankton samples with the methane that was released during the oil spill?
- Describe the pathways that scientists believe led to methane from the spill entering the food web.
- Why is it difficult to say with certainty that the carbon found in planktonic organisms originated from the Macondo well?

Questions

1. What is the carbon cycle and how does it affect ocean processes. *Answers will vary.*
2. What is methane? Is it a liquid, gas, or solid? *A colorless, odorless, combustible gas.*
3. What is a marine food web? How is it affected by the carbon cycle? *Answers will vary.*
4. Where did the methane released from the spill come from? *A byproduct of the formation of crude oil.*
5. Describe the pathway that methane used to enter the food web. *Methanotrophy.*

Extension

Divide the class into study groups. Assign each group an ecosystem (estuary, coastal shelf, deep sea). Each group should then create a food web for their study site. Include as many components as they can identify. The students should then share their findings with the class.

Resources & References

Background Information on the Carbon Cycle from NASA
http://earthobservatory.nasa.gov/Features/CarbonCycle/

ECOGIG Research: Plankton and Water Column Dynamics
https://ecogig.org/plankton-water-column-dynamics

ARTICLE REPRINT

Study Confirms Methane-Eating Bacteria Contributed to Carbon Entering Food Web

Posted online January 14, 2014

Source: GoMRI http://gulfresearchinitiative.org/study-confirms-methane-eating-bacteria-contributed-carbon-entering-food-web/

Scientists confirmed that methane-derived carbon, likely from the Deepwater Horizon oil spill entered the food web via small particles through a pathway known as methanotrophy.

Bubbles of methane gas rise through a mussel bed at the Pascaguola Dome. (Image courtesy of the NOAA Okeanos Explorer Program)

They published their findings in the December 2013 issue of Environmental Science and Technology Letters: **Fossil carbon in particulate organic matter in the Gulf of Mexico following the Deepwater Horizon event**.

The 2010 Gulf oil spill released large volumes of both oil and methane. Above water measurements at the time indicated that little of this methane went into the atmosphere, suggesting that the majority of it remained in the water column. Summarizing findings from his **2012 study**, Chanton said they found "approximately 5-15% of the carbon-composing plankton collected in 2010 and 2011 could be attributed to carbon released by the oil spill" with "smaller size plankton appearing to have more petro-carbon in it" and that "methane (rather than oil) seemed a more likely avenue for the intrusion of petro-carbon into the food web."

In this 2013 study, scientists report that tiny particles floating in the deep Gulf water column have organic carbon in them that matches the carbon released as methane from the Deepwater Horizon spill. Chanton estimates that "28 to 43% of the carbon in these particles is from fossil methane from the spill." The team used carbon isotopes (^{13}C and ^{14}C) to match carbon from methane with carbon in plankton and floating particles. Both studies show that the amount of oil spill carbon increases as the size of things gets smaller because floating particles are smaller than plankton.

These methane-eating bacteria (methanotrophs) are very efficient in converting the gas into biomass. Chanton explained that "methanotrophic transfer to biomass can be as great at 40-50%" as compared to "more traditional food webs where trophic transfers that are generally about 10% – meaning that 90% of the food consumed is lost to produce energy and carbon dioxide." He also said that this high transfer rate of methane into biomass is "significant and allows the highly successful symbiotic relationship of methanotrophic bacteria with seep fauna, particularly mussels." The researchers believe that this appears to be true for the wider Gulf, too. Chanton said, "As much as 40% of the methane released from the spill went into bacteria, which then became small particles ingested by plankton."

The team described their model for this process as methane → bacteria → particles → plankton.

In their discussions, the researchers stated that the carbon which entered the food web is "likely associated with the Macondo oil spill" but they also note that lack of prior "background" data regarding the ^{13}C and ^{14}C levels of particulate organic carbon in the area makes it difficult to determine the relative importance of natural seepage effects. Nonetheless, this study's results are consistent with the earlier hypothesis (Chanton et al.) "that a small size fraction of ^{13}C- and ^{14}C-depleted carbon affected the planktonic food web and this fraction was likely affected by methanotrophy."

The study's authors are J. Cherrier, J. Sarkodee-Adoo, T. P. Guilderson, and J. P. Chanton (Environmental Science and Technology Letters, 2013).

LESSON PLAN:
Oiled Marine Snow

How oil travelled from the surface to the seafloor

Note: See *Resources* (page 50) for where to order the chemicals needed for this lab.

Objective: To increase students understanding of the chemical process that influenced the settling of oiled marine snow on the seafloor.

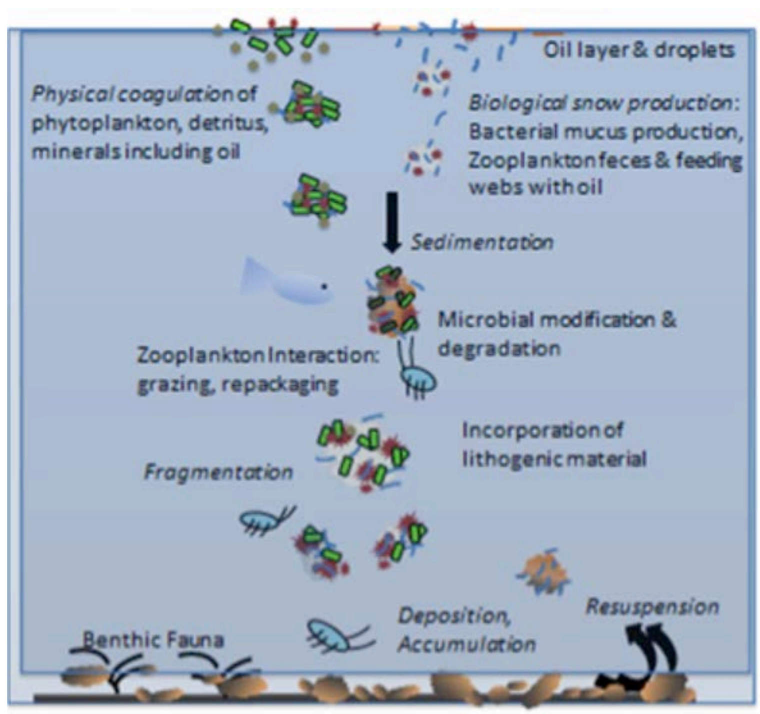
Standards: OLP 5, 6; SC.912.E.7.1

Time Required: One 50-minute class period

Keywords: marine snow, flocculation, upwelling

Materials:
- Copies of the article, "*Study Explains Pathways for Oiled Marine Snow Formation"* (see page 50)
- "Muddy water" (add one cup of dirt to 1 liter of water) or pond water with suspended particulate matter (500mL per demonstration)
- Alum solution (1 tsp potassium aluminum sulfate or ammonium aluminum sulfate to 1 liter of water)
- Stirring rod
- Jars or beakers (one for each group)
- Limewater (3 tsp calcium hydroxide in 1 liter of water)
- Two jumbo (15 ml) transfer pipettes (one set for each group)
- Litmus paper, pH indicator paper (one for each group)

Background



Source: Dr. Jeff Chanton, Florida State University

Marine snow is organic material including dead animals and plants as well as sediment and fecal matter that is produced in the photic zone of the ocean, where sunlight penetrates and allows phytoplankton, the primary producers in the ocean, to thrive. Marine snow travels from the highly productive photic layer down to the seafloor where sunlight cannot penetrate, and is the major food source for many of the deep ocean inhabitants. The amount of marine snow changes with surface productivity. Marine snow is decomposed into nutrients by bacteria as it sinks to the ocean floor. **Upwelling** brings the nutrients as food up to the phytoplankton thus completing the cycle of matter and flow of energy in the open ocean food chain. **Flocculation** is the process by which particles mix with other particles that cause them to coagulate (thicken and become solid). Often flocculation is accompanied by an accelerated rate of settling on the seafloor. Oil from the 2010 Deepwater Horizon oil spill is thought to have mixed with plankton and sediment to form oiled marine snow. In order to gain an understanding of the mechanisms that contribute to oiled marine snow, students will read an article on its formation and conduct a lab demonstrating the process of flocculation.

Procedure

1. **Read Article:** Have students read the article, *"Study Explains Pathways for Oiled Marine Snow Formation"* and answer the following questions:
   - What is marine snow? And is the formation of marine snow a common ocean process?
   - What contributes inorganic particle inputs to the northern Gulf of Mexico?
   - The experiments demonstrated the potential of __________-mediated or __________-aggregate snow to transport oil to the seafloor.
2. **Watch ECOGIG's video on Marine Snow** https://www.youtube.com/watch?v=EfeNlavFmlk (4:30min)
3. **Flocculation Lab:** (Adapted from *"Things that Matter to Flocculants"* from USF)
   Prior to class prepare an alum solution (1 tsp potassium aluminum sulfate or ammonium aluminum sulfate to 1 liter of water) and a limewater solution (3 tsp calcium hydroxide in 1 liter of water). Lay out materials for each group.

   Break students up into groups of 3-4 and explain that they will be conducting a lab to determine how oil mixed with other particles to form marine snow. Have students complete the following:
   - Prepare a jar with muddy water (add one cup of dirt to 1 liter of water)
   - Add a transfer pipette full of the lime solution to the muddy water
   - Dip a piece of pH indicator paper into the beaker and observe the color. If the litmus paper turns blue, the solution is basic. If it stays red, add more lime solution.
   - Add a pipette full of alum solution to the muddy water mixture. Observe for a moment. If nothing happens, add another pipette full of alum.
   - A thick precipitate will form and begin to settle out.

   Have students answer the following questions:
   - Describe the process that caused the particles in the water to coagulate after the alum solution was added.
   - What implications does this have for the flocculation that occurred after the Deepwater Horizon oil spill?

Questions

1. How is marine snow formed? *Organic material that is produced at the surface and than falls to the seafloor.*
2. Explain the role of flocculation and sedimentation in the ocean ecosystem. *Helps with transport of materials.*
3. How might oil from the Deepwater Horizon spill reach the bottom of the seafloor? *Flocculation and sedimentation.*

Extensions

Repeat the flocculation experiment using a mixture of oil and sediment instead of muddy water to demonstrate how oil and sediment mixed in the ocean environment.

Combine this lesson with a filtration lab.

Resources & References

Carolina Biological Supply (A source for the chemicals needed to complete this lab) http://www.carolina.com

ECOGIG Marine Snow Video https://www.youtube.com/watch?v=EfeNlavFmlk

Things that Matter to Flocculants
https://www.teachengineering.org/view_activity.php?url=collection/usf_/activities/usf_flocculant/usf_flocculant_activity01.xml

ARTICLE REPRINT

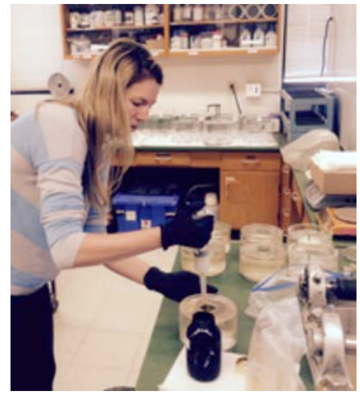
Study Explains Pathways for Oiled Marine Snow Formation

Posted online March 24, 2015

Source: GoMRI, http://gulfresearchinitiative.org/study-explains-pathways-for-oiled-marine-snow-formation/

University of California Marine Science Institute researcher Uta Passow investigated the formation of aggregated oil and organic material, commonly called marine snow, after the Deepwater Horizon spill.

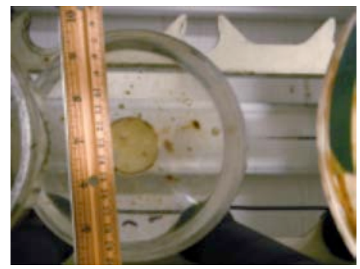
She found that microbes and plankton had distinct interactions with oil, subsequently providing alternate marine snow development pathways, and that the presence of Corexit likely inhibited the formation of microbial-generated marine snow. Passow published her findings in the October 2014 issue of Deep Sea Research II – Topical Studies in Oceanography: **Formation of rapidly-sinking, oil-associated marine snow**.



Lab manager Julia Sweet prepares treatments for the rolling tanks experiments (Photo provided by: Uta Passow)

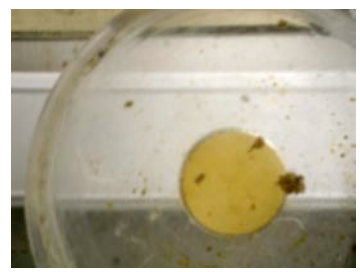
The formation of marine snow, which are sinking composite particles greater than 0.5 millimeters, is a common ocean process that rapidly transports particles from surface waters to the sea floor. The continental shelf topography of the northern Gulf of Mexico facilitates a suspended sediment zone. Additionally, the northern Gulf receives inorganic particle inputs from rivers, run-off, and coastal erosion. These subsurface conditions along with natural hydrocarbon seafloor seeps provide an environment favorable for the formation and sinking of oiled mineral aggregates.

Macondo oil accumulated at the sea surface and in subsurface plumes. Prior research has documented observations of large (millimeter to centimeter sized) sinking marine snow near surface slicks from the spill (**Passow, et al., 2012**) and flocculent oily material that coated coral reefs near the spill site (**Fisher, et al., 2014**). In this study, Passow used roller table experiments to investigate the conditions that induce marine snow and the effects of oil type (Louisiana light crude, Macondo oil, and bucket-collected spill oil), photochemical weathering, and phytoplankton and dispersant presence on its development.



Diatom oil aggregate. (Image credit: Julia Sweet)

Seawater treatments, with no particles greater than one millimeter present, incubated with collected spill oil formed centimeter-sized marine snow rich with microbial-generated mucus. Smaller, yet similar, marine snow formed in incubations with weathered crude oil. Marine snow formed even when spill oil was added to artificial seawater, suggesting that the oil included the microbial community responsible for snow formation.



Microbial oil aggregate. (Image credit: Julia Sweet)

Phytoplankton presence in seawater treatments resulted in appreciable carbon amounts (16%-65%) incorporated in diatom aggregates, independent of oil type. However, the oil type did affect aggregates' appearance, size, and dynamics and likely increased the stability, cohesion, and sinking speed of these plankton aggregates.

Low concentrations of Corexit 9500A in treatments slowed, reduced, or completely inhibited microbial-mediated snow production. Conversely, higher dispersant concentrations produced buoyant oil aggregates that did not sink, suggesting that the oil contributed to the cohesion and stability of Corexit-mediated aggregates.

Passow explained that "this study contributed a central piece towards the understanding of the mechanisms that lead to oil-sinking products." In her discussions, she said that microbial-mediated marine snow may provide a potentially effective mechanism for surface oil removal. While acknowledging the difficulty in currently assessing Corexit's overall effects on oily marine snow, she suggested that Corexit likely reduced post-spill snow perhaps by impacting bacterial exudates or promoting a shift in less mucus-generating strains.

Microbial oil snow. (Image credit: Julia Sweet)

These experiments demonstrated the potential of microbial-mediated or plankton-aggregate snow to transport oil carbon to the seafloor. Passow recommends that future modeling efforts and oil spill budget calculations should include marine snow as an oil distribution mechanism and include inputs on microbial and phytoplankton populations and oil weathering rates. Additionally, scientists should re-evaluate dispersants as a mediating measure.

Oil-associated marine snow formation and its subsequent transport is the focus of a larger dedicated effort. Passow explained, "MOSSFA (Marine Oil Snow Sedimentation and Flocculent Accumulation) is a working group that facilitates investigations of processes leading to the observed seafloor oil accumulation. Founded in May, 2013, the MOSSFA working group organized a **workshop**, **town hall meeting**, and continues to hold smaller topic-specific meetings. Recently-funded consortia and the MOSSFA group are working together towards a new marine snow research phase."

LESSON PLAN:
What can we learn from sediment profiling?

Determining the fate of oil in the sediment

Note: This lesson plan works best in conjunction with, "*Sifting through the Sediment*" lesson in the Geomorphology module (page 30).

Objective: To introduce students to sediment cores, sediment profiling, and the sediment research that is being conducted in the Gulf of Mexico.

Standards: OLP 2, 5; SC.912.E.6.4, SC.912.E.6.5, SC.912.E.6.6, SC.912.N.1.1

Time Required: One or two 50-minute class periods

Keywords: sediment, sediment profiling, sediment core, multi-corer

Materials:

Note: You will need enough materials for groups of 3-4 to do the lab twice.

- 3 wide-mouth containers
- 2 measuring cups (or small paper cups)
- Coarse-grained sand or gravel
- Medium- to fine-grained sand
- Clay or mud
- Glass, jar, or paper cup to use as a stamp
- Molasses
- Mineral oil
- Copies of the article, *"Study Reveals Oil Spill Changed Oxygen Conditions in Gulf Sediment"* (page 55)

Background

The **sediment** at the bottom of the seafloor can hold clues to the chemical processes that occur in the ocean. Scientists take core samples of the sediment using a device called a **multi-corer** to determine the chemicals present, how they are degrading over time, and the effect of these chemicals on the ocean food chain. After the 2010 Deepwater Horizon oil spill, researchers hypothesized that a large percentage of the spilled oil may have accumulated in the sediments and were potentially being recycled and incorporated into the ecosystems that inhabit the seafloor from microbes to predators. Scientists are looking at the impact on sediment composition as well as the organisms that live in the sediment.

Still shot of the multi-corer as it retrieves sediment cores on the seafloor. Taken during a Deep-C research cruise. Photo credit: Ian MacDonald (FSU).

By analyzing existing baseline data from previous core sampling expeditions and comparing the results with **sediment cores** collected since the spill, researchers at FSU and USF have been able to identify potential changes in sediment characteristics related to the Deepwater Horizon oil spill. It is hypothesized that these changes were due to the influx of hydrocarbons that fueled a major biogenic bloom in northeastern Gulf of Mexico surface waters and ultimately led to high sediment accumulation rates.

Sediment retrieved from the seafloor during a Deep-C research cruise. The note next to the sample denotes the date and location that the sediment was retrieved from.

Sediment cores retrieved during several Deep-C research cruises provide unique natural archives with the potential to accurately record the biological and chemical processes and the environmental conditions that existed prior to oil drilling, through the Deepwater Horizon oil spill, and including the eventual environmental and ecosystem recovery. These archives will provide vast amount of baseline data to analyze the state of the Gulf of Mexico for years to come. Deep-C's analytical work includes core photography, grain size analysis, bulk density determinations, stable isotope analysis, and radiocarbon analysis of bulk sediments among other things. Researchers at several institutions are using experimental approaches to evaluate the fate of buried Deepwater Horizon oil including tracking the degradation of oil in near shore and off shore environments and using the radioactive isotope, carbon 14, to detect the presence of oil on the seafloor. In this lesson, students will read an article on information gained from sediment profiling of the northern Gulf of Mexico seafloor, see the tools of the trade in action, and conduct a sediment penetration activity to determine oils ability to penetrate the seafloor.

Procedure

1. Research: In small groups or individually, have students research the sources of sediment in the Gulf of Mexico and write a 500-word report on their findings. Report must include at least three different sources of sediment in the Gulf and an explanation of the pathways. Students should cite their sources.

2. Article: Have students read the article, "Study Reveals Oil Spill Changed Oxygen Conditions in Gulf Sediment" and answer the following questions:

- What was the purpose of this study?
- How did researchers track changes to the natural cycle?
- When were the sediment cores used in this study collected?
- Describe the differences between the pre- and post-spill metal concentrations in sediment cores.

3. Videos: Show students the following two videos to illustrate some of the methods researhers use to collect sediment samples for analysis:

- Multi-corer Test Video: https://youtu.be/gRt2icfYYZ0
- ECOGIG Sediment Traps Video: https://ecogig.org/content/sediment-traps-2

4. Lab: Divide students into groups of 3-4 and pass out lab materials. Explain that you will be performing an experiment to see how oil penetrates a variety of sediments. Run the experiment twice, once using dry sediment and once with wet sediment, and then compare results. This can also be done as a demonstration.

1. Each group should have three wide-mouthed containers, one each of dry coarse sand, fine sand, and clay/mud, which are about two-thirds full.
2. Instruct students to press the bottom of a small glass, jar, or paper cup into two places on the surface of the sediment to make two treatment areas in each container.
3. Next, measure out equal volumes of molasses and mineral oil into the two cups
4. Choose one of the containers. Pour the molasses into one of the treatment areas, and mineral oil into the other.
   - Observe the immediate behavior of the liquids. Do they penetrate the sediment? How fast does this happen? What differences between the two liquids do you see?
5. Repeat these steps for the other two containers then compare.
6. Repeat steps 1-5 using wet sediment.
7. Answer the following questions: Which penetrated faster? Is the Deepwater Horizon oil more like the molasses or the mineral oil? What can we infer about this in terms of the rate of crude oil sediment penetration? Which sediment allowed the liquid to penetrate the quickest? Slowest? Why?

Questions

1. What is a sediment core? *A section of sediment extracted from the ground as a tube.*
2. What is sediment profiling? *A methodology used to analyze sediment cores.*
3. How is it useful in conducting scientific research? *Answers will vary.*
4. Describe two methods that scientists use to collect sediment samples. *Multi-corer, sediment trap, etc.*
5. What have scientists studying the Deepwater Horizon oil spill learned from sediment profiling? *Hydrocarbons caused a bloom.*

Extensions

Combine with the "*Sifting through the Sediment*" lesson in the Geomorphology module (page 30).

Conduct a porosity lab.

Investigate sediment core repostiories and see if they will send you a sample to analyze as a class.

Resources & References

Columbia University Sediment Core Repository
https://www.ldeo.columbia.edu/core-repository

Coleman, F., Chanton, J., & Chassignet, E. (n.d.). Ecological Connectivity in the Northeastern Gulf of Mexico. *International Oil Spill Conference Proceedings*, 2014(1), 1972-1984. doi:10.7901/2169-3358-2014.1.1972

ARTICLE REPRINT

Study Reveals Oil Spill Changed Oxygen Conditions in Gulf Sediment

Posted online May 26, 2015
Source: GoMRI, http://gulfresearchinitiative.org/study-reveals-oil-spill-changed-oxygen-conditions-in-gulf-sediment

A team of scientists from Eckerd College and University of South Florida conducted a time-series sediment study to better understand impacts from the Deepwater Horizon oil spill.

Three years post-spill, they found a continued state of altered geochemical conditions in sediment near the spill site. Concentrations of manganese, rhenium, and cadmium in sediment indicated a large organic carbon influx and subsequent decreases in oxygen concentrations. Decreases in the density of benthic foraminifera coincided with these altered conditions, suggesting potential impacts on benthic ecosystems. The researchers published their findings in Deep Sea Research Part II: Topical Studies in Oceanography: **Changes in sediment redox conditions following the BP DWH blowout event**.

Using a multi-core sediment sampler, David Hastings recovers sediment cores from the Northern Gulf of Mexico. (Photo credit: David Hastings, Eckerd College)

During and after the oil spill, scientists observed increased microbial activity and the forming, sinking, and settling of hydrocarbon enriched marine snow on the sea floor. The purpose of this study was to improve understanding about the association of these biological responses to the large hydrocarbon influx from the oil spill and identify potential impacts on the deep ocean environment.

Researchers analyzed concentrations of metals that indicate low oxygen and anoxic conditions as a means to track changes to the natural cycle that takes place when carbon gradually settles on the ocean's floor and slowly becomes incorporated into sediment. Peaks in manganese indicate the upper boundary of a geochemical cycle in sediment known as redoxcline. Enrichments of rhenium and cadmium indicate low oxygen or reducing conditions beneath that upper boundary of manganese.

After recovering sediment cores from the Gulf, Hastings removes the sediment core from the sampler. Frequently, the cores are extruded on board the ship. (Photo credit: David Hastings, Eckerd College)

The team established pre-spill baseline profiles of manganese, rhenium, and cadmium using sediment cores collected in 2007 and 2009 and two weeks after the oil spill, prior to the substantial organic carbon sedimentation that scientists observed in the months following the spill. They determined post-spill profiles of these metals using sediment cores collected between August 2010 and August 2013.

Pre-spill concentrations of these metals were typical of continental slope sediments. Post-spill metal concentrations showed noticeable differences in the top 5-30 millimeters of sediment, with rhenium concentrations three to four times higher than background levels. These metal enrichments demonstrated a change in post-spill sediment conditions, likely as a result of organic carbon remineralization.

The team analyzed benthic foraminifera that live in the upper sediment layers as potential indicators of impacts from shifting redoxcline conditions. Decreases in the density of benthic foraminifera were coincident with the changes in metal concentrations at the same depth range. In December 2010 there was a 40-60% reduction in the two most abundant genera of benthic foraminifers, and in February 2011 there remained a reduction in the genera.

In their discussion, the researchers noted that the more subtle changes in manganese, rhenium, and cadmium concentrations deeper in sediment suggest that a **marine snow event** associated with the oil spill likely contributed to the changed conditions closer to the seafloor. Diminishing rhenium and cadmium concentrations in sediment cores collected in the third year may signal a return to pre-spill conditions. Continued assessment of metal concentrations can help describe the temporal evolution of sediment conditions and document potential long-term effects as well as a possible return to background conditions.

This study's authors are D.W. Hastings, P.T. Schwing, G.R. Brooks, R.A. Larson, J.L. Morford, T. Roeder, K.A. Quinn, T. Bartlett, I.C. Romero, and D.J. Hollander.

LESSON PLAN:
Oil Weathering and Fingerprinting

Investigating how oil breaks down over time

Objectives: Students will learn about oil spill forensics and develop an understanding of how oil breaks down over time. They will also learn how scientists use gas chromatography to separate oil molecules.

Standards: OLP 1,6; SC.912.L.17.2, SC.912.L.17.16, SC.912.N.1.6

Time Required: One or two 50-minute class periods

Keywords: chromatography, solvent, analyte, retention factor, oil fingerprinting, chromatogram, oil weathering

Materials:

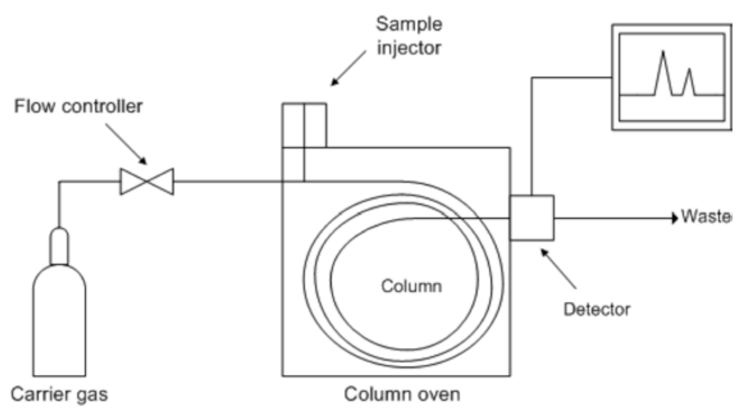
- Chromatography paper or coffee filters
- Three different black pens (analyte) (e.g. Crayola marker; Sharpie; Vis-a Vis)
- Rubbing alcohol (solvent)
- Flat toothpicks
- Small plastic or glass cups
- Ruler
- Calculator

Background

Oil is the result of plant debris and prehistoric organisms that have been heated and compressed ("cooked and squeezed") over millions of years – a process that changed their chemical composition, eventually transforming them into oil. Oil from around the world has different properties. Yet, even oils made in the same general area will have unique characteristics and can be definitively matched. So similar to the way that a crime scene investigator can look at fingerprints to identify a suspect…scientists can look at the distinct **"fingerprints"** or "genetic markers" of oil and determine its origin, much like a forensic investigator analyzes DNA.

One of the ways we can determine the fate of oil released into the environment is to study an effect called **"weathering"** — that is, how oil changes over time due to natural processes such as sunlight or microbial degradation. Oil is made up of many different compounds and weathering affects each of its properties in different ways.

Chromatography is a precise laboratory technique that allows scientists to analyze oil by separating the molecules contained in a sample. Analytical chemistry uses chromatography to conduct qualitative analysis (identify the components) and quantitative analysis (determine the concentration) of unknown substances. By separating a molecule from the oil mixture, it can be isolated and quantified. The different peaks on a **chromatogram** (the visualization of the data collected) correspond to different components in the sample and allow for tracking the fate or extent of weathering of many compounds. In the following lesson students will read a paper on oil spill forensics, locate data on analyzed oil samples from Woods Hole Oceanographic Institution (WHOI), and conduct a paper chromatography lab.



Gas Chromatography

Source: http://commons.wikimedia.org/wiki/File:Gas_chromatograph-vector.svg

Procedure

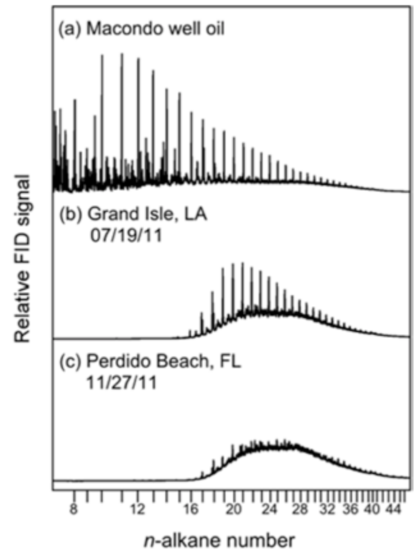
1. Have students read the article "Study Describes Use of Oil Fingerprinting to Identify Source of 2012 Gulf Sheen" and answer the following questions:

- *Where did the oil that the scientists from WHOI are studying originate?*
- *What is the name of the analytical instrument scientists developed to more effectively separate oil molecules?*
- *Describe the mechanism that scientists believe caused the oil sheen.*
- *What is a biomarker and why is it significant?*

2. Comparing Chromatograms Lab. Direct students to the WHOI Gulf Coast Sample Repository (https://www.whoi.edu/page/live.do?pid=73756) and have them select samples from three different states to compare (see example at right). Make sure that the samples selected have a linked chromatogram. Ask students to compare and contrast the three samples and answer the following questions:

- *What is the same?*
- *What is different?*
- *What could account for the differences?*
- *Why is this sort of precise information about oil weathering useful for scientists?*

Repeat activity using three different time frames (i.e. 2012, 2013, 2014).



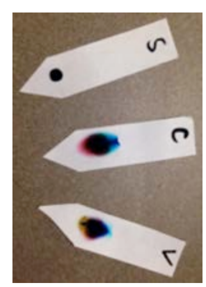
Gas chromatographic traces from the Deepwater Horizon as well as samples from Louisiana and Florida. The samples found clearly show that nature has changed the composition relative to the original oil but also that weathering is different in the Grand Isle sample vs. Perdido Beach, even though both were collected at nearly the same time. Source: Chris Reddy, WHOI

3. Paper Chromatography Lab

(Adapted from: "Ink Chromatography", Museum of Science & Industry Chicago, IL)

In this lab, students will be separating the pigments that make up the color of three black pens. The ink acts as the **analyte** (the substance to be analyzed) and alcohol is the **solvent**. As the alcohol moves up the paper, the dye molecules from the ink mixture will move with it. If they are more strongly attracted to the alcohol molecules than to the paper molecules, the dyes will continue to move up the paper. If the dye molecules are more strongly attracted to the paper than the alcohol, they will move more slowly than the alcohol or not at all. Each paper chromatogram displays a unique pattern formed by the separation of the visible bands of dyes. After running the chromatogram, each separated band can be assigned a **Retention factor (Rf)** which is characteristic of each specific dye(s). The Rf is a ratio of the distance the band of color travels to the distance the solvent (alcohol) travels. The Rf is calculated by dividing the band distance by the solvent distance.

1. Pour 10ml of rubbing alcohol into a small cup.
2. Cut a strip of filter paper to form a point at one end.
3. Choose a marker and make a dot above the pointed end. Record the brand of marker by initialing the top of the filter paper.
4. Lower the pointed end of the paper into the solvent. Make sure the dot stays above the solvent level.
5. Wait for the solvent to rise toward the top of the paper.
6. Once solvent has finished moving up the strip, (usually takes 3-5 minutes) remove the paper from the cup and mark with a pencil the highest point the solvent traveled.
7. Let the strip dry and tape it to the chart on the following page.
8. Fill in the sections on the Lab Sheet. To calculate the retention factor divided the distance the pigment travelled by the distance the solvent travelled.



Results from an ink chromatography experiment using three different black markers.

Ink Chromatography Lab Sheet

Tape Strip Here	Tape Strip Here	Tape Strip Here
Total # of colored pigments	Total # of colored pigments	Total # of colored pigments
Solvent distance measured	Solvent distance measured	Solvent distance measured
Colored Pigment #4 __________ Color Distance Measured __________ Rf __________	Colored Pigment #3 __________ Color Distance Measured __________ Rf __________	Colored Pigment #4 __________ Color Distance Measured __________ Rf __________
Colored Pigment #3 __________ Color Distance Measured __________ Rf __________	Colored Pigment #4 __________ Color Distance Measured __________ Rf __________	Colored Pigment #4 __________ Color Distance Measured __________ Rf __________
Colored Pigment #2 __________ Color Distance Measured __________ Rf __________	Colored Pigment #2 __________ Color Distance Measured __________ Rf __________	Colored Pigment #2 __________ Color Distance Measured __________ Rf __________
Colored Pigment #1 __________ Color Distance Measured __________ Rf __________	Colored Pigment #1 __________ Color Distance Measured __________ Rf __________	Colored Pigment #1 __________ Color Distance Measured __________ Rf __________

Questions

1. What is oil spill forensics and what are some of the tools that scientists use to fingerprint oil?
2. How does ink chromatography relate to oil fingerprinting?
3. What are other mixtures that could potentially be separated by gas chromatography?
4. What are biomarkers? How could they potentially degrade over time?

Extensions

Contact a nearby university to see if anyone working with gas chromatography and could show your class.

Conduct a leaf chromatography experiment (See: http://www.msichicago.org/online-science/activities/activity-detail/activities/see-the-colors-in-leaves/)

Resources & References

Ink Chromatography Lab -
http://www.msichicago.org/fileadmin/Education/learninglabs/lab_downloads/EL_ink_chromatography.pdf

NOAA Tar Ball Fact Sheet - http://www.noaa.gov/factsheets/new%20version/tar_balls.pdf

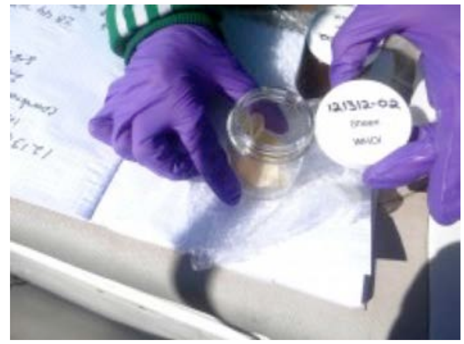
ARTICLE REPRINT

Study Describes Use of Oil Fingerprinting to Identify Source of 2012 Gulf Sheen

Posted online August 12, 2013
Source: GoMRI, http://gulfresearchinitiative.org/study-describes-use-of-oil-fingerprinting-to-identify-source-of-2012-gulf-sheen/

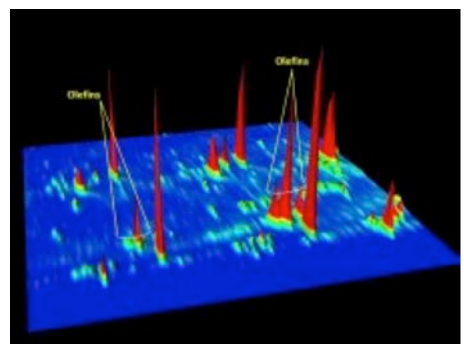
Scientists from Woods Hole Oceanographic Institution and University of California, Santa Barbara used a novel fingerprinting technique to identify the source of oil sheens that appeared in late 2012 near the site of the *Deepwater Horizon* disaster.

The sheens contained a mixture of Macondo well oil and alkenes (commonly called olefins) that are used in drilling operations. Researchers found that the sheens most likely came from pockets of Macondo well oil that were on the rig before it exploded and are now in the debris field on the ocean floor. They also showed conclusively that the oil was not leaking from the Macondo well which was "shut-in" in the summer of 2010. They published their findings in the June 2013 issue of *Environmental Science & Technology*: **Recurrent oil sheens at the Deepwater Horizon disaster site fingerprinted with synthetic hydrocarbon drilling fluids**.



After researchers retrieved oil-coated screens used to collect samples from surface sheens, each screen was sectioned into several pieces for analyses. Some were reserved for DNA extraction; others analyzed for drilling fluids and shared with the National Oceanic Atmospheric Administration for standard petrochemical analyses. (Photo by Christoph Aeppli, WHOI)

In mid-September 2012, the US Coast Guard received reports from BP of oil sheens near the site of the *Deepwater Horizon* incident. There was concern that the Macondo Well, capped in July 2010, might be leaking. Identifying the source of the oil was important because of environmental and legal issues and also to estimate the magnitude of the problem and inform the response process.



Chemical compounds present in an oil sheen sample, highlighting the alkene or olefin fingerprint. (Credit: Robert Nelson, Woods Hole Oceanographic Institution)

This study's research team has been analyzing the chemical makeup of *Deepwater Horizon* oil since the incident began. Several years before the incident, they patented a highly-sensitive and accurate method to detect and identify alkenes found in drilling fluids (lubricants that aid the process of drilling for oil) using "comprehensive two-dimensional gas chromatography." They developed this patent for the petroleum industry, but this was the first time they used this technique to address an environmental issue. Since drilling-fluid alkenes are not present in crude oil or natural seeps, and thus not in the oil that was released from the broken blowout preventer (drilling operations were over at that time), being able to identify these alkenes provided the team with a means to use them as a fingerprint to determine the sheens' source.

The team collected 14 samples (taken in October and December, 2012) from the new sheens. They compared these samples to oil and chemicals from the Macondo well, the cofferdam (the device used in an attempt to cover the Macondo well in May 2010), drilling fluids, oil slick and oiled field samples, and floating rig debris (a broken piece of the riser assembly collected in May 2010 which had drilling fluids). Analysis of chemical biomarkers (measurable characteristics that indicate the presence of a chemical compound) showed the presence of Macondo well oil and drilling-fluid alkenes in all sheen samples and in the floating rig debris. There were no alkenes in oil from the cofferdam or in beach samples that the team have been collecting and analyzing since the disaster. These findings pointed to the source of the sheens as most likely "an oil/drilling mud mixture [that] originated from the DWH wreckage site" and that the source was a "finite volume of oil, rather than a leaking well." The researchers also analyzed the spatial pattern of how the sheens evaporated, looking for areas with the least amount of evaporation. They determined that the sheens "surfaced closer to the DWH wreckage than the cofferdam site."

In their discussions, researchers suggest that “drilling mud olefins are a powerful forensic tool” and “provide a framework for assessing the fate of drilling fluids released during hydrocarbon exploration and other activities around the globe.”

Additionally, researchers described this work as having another “victory.” They, as members of academia, were able to play a key role with multiple stakeholders, working closely with industry (BP) and federal agencies (U.S. Coast Guard, NOAA). The science team operated with transparency, alerting the government and BP about their research plans. All stakeholders sought to determine the source of the oil, though each required a different level of certainty about the results, and each had different questions to answer.

Dr. Christopher Reddy said, “The long lasting impacts of this effort were highlighting that academia can play a useful role during a crisis. We can be unbiased and collaborative without losing our integrity. What is lost on many of our colleagues is that interacting with representatives of the government and BP provided advice and input that improved our research. This is a win-win.”

The study authors are Drs. Christoph Aeppli, Christopher M. Reddy, Robert K. Nelson, Matthias Y. Kellermann, and David L. Valentine (*Environmental Science & Technology,* 2013, 47 (15), 8211–8219).

The research team’s second sampling expedition in December 2012, was more challenging due to the close proximity of a BP survey vessel, Olympic Triton, which was operating two ROVs, and a mobile offshore deep drilling unit. The rig and vessel each require a reasonable stand-off distance for safety precautions. WHOI’s Chris Reddy is shown here, with the drilling rig behind him. (Photo by Christoph Aeppli, Woods Hole Oceanographic Institution.)

Geochemistry Quiz

1. What is salinity and how is it measured?

2. Describe how biogeochemical cycles affect ocean processes.

3. What is the carbon cycle and how does it affect ocean processes?

4. Describe the pathway that methane used to enter the food web.

5. How is marine snow formed?

6. Explain the role of flocculation and sedimentation in the ocean ecosystem.

7. What is sediment profiling?

8. Describe two methods that scientists use to collect sediment samples.

9. What is oil spill forensics and what are some of the tools that scientists use to fingerprint oil?

10. What are biomarkers? How could they potentially degrade over time?

Geochemistry Glossary

Analyte: a substance whose chemical constituents are being identified and measured

Biogeochemical cycles: the process by which chemicals move through the other earth cycles

Carbon cycle: the movement of carbon through the different spheres of the Earth

Chemical processes: the processes that cause chemical to combine and break apart

Chromatogram: the visual result of conducting chromatography

Chromatography: laboratory techniques used to separate mixtures

Flocculation: the process by which individual particles clump together

Marine food web: a system of interlocking and interdependent food chains in the marine environment

Marine snow: decomposed or waste materials that slowly sink to the bottom and serve as a food source for deeper water animals

Methane: an odorless, colorless, combustible gas (CH_4)

Methanotrophy: the use by bacteria of methane as a food source

Multi-Corer: a tool used to extract sediment cores from the seafloor

Oil fingerprinting: a methodology used to pinpoint where an oil spill came from

Oil weathering: the process by which oil is weathered over time by the earths systems

PPT (parts per thousand): the common measurement for salinity

Retention factor: the amount of the analyte that is retained in during chromatography

Salinity: the dissolved salt content of a body of water

Sediment: a naturally occurring material that is broken down by processes of weathering and erosion

Sediment core: a section of the ground that is extracted as a tube for analysis

Sediment profiling: a method of analyzing sediment for information

Solvent: a substance that dissolves a solute (a chemically different liquid, solid, or gas), resulting in a solution

Upwelling: a process in which deep, cold water rises toward the surface