Oil Spill Summit II: Chemical Considerations

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Organized by: South Atlantic Sea Grant College Programs
Summary by: The Georgia Coastal Research Council

Photograph by Chris Graythen, Getty Images (http://news.nationalgeographic.com/news/)

Background

The Deepwater Horizon (DH) well rig explosion at the Macondo Prospect in the Gulf of Mexico on April 20th 2010 caused one of the worst oil spills in U.S. history. By the time the well was capped on July 15th 2010, an estimated 4.9 million barrels of oil were discharged from the failed well, located some 40 miles off the coast of Louisiana at a depth of 5,000 feet. Although there are immediate and acute effects of this disaster in the Gulf of Mexico itself, there is also concern that the oil and associated dispersants from this incident will affect other areas. On June 9th 2010, the South Atlantic Sea Grant programs gathered a panel of physical oceanographers for an Oil Spill Summit. During the summit, the panel discussed what is known about circulation patterns in the region and the various mechanisms by which contaminated water might be transported out of the Gulf of Mexico to the east coast of the U.S. On June 29th 2010, the South Atlantic Sea Grant programs convened a second summit, this time with petrochemical and chemical oceanographic experts from the region. This panel met at the University of North Florida to discuss the chemistry of the DH material that might reach the East Coast (see Appendix A for a list of participants). This report, Oil Spill Summit II: Chemical Considerations, is a technical summary of the material discussed at the meeting.

Discussion at the summit focused on three main areas: I) the properties of the compounds being released from the Gulf of Mexico spill site, II) the processes that will likely affect their form and composition before they reach the southeastern U.S., and III) recommendations for monitoring the presence of DH material in the region.

I. Deepwater Horizon Well Material

a. Crude Oil
Crude oil contains a mixture of different types of hydrocarbons, which are compounds that contain primarily hydrogen and carbon. The hydrocarbons in crude oil can be of different sizes (ranging varies from 1 to 50 carbon atoms per molecule) and structures (ranging from simple linear alkanes to branched or cyclic molecules). Some are complex structures such as polyaromatic hydrocarbons (PAHs) that are known to have deleterious effects on humans and the environment. Heterocyclic compounds that incorporate additional elements, such as oxygen, nitrogen, or sulfur can also be present. The petroleum from the DH well is considered to be a typical South Louisiana crude oil, which is defined as a "light", "sweet" mixture. "Light" refers to the fact that the material has a low density, due to the relatively high abundance of smaller, saturated alkane hydrocarbons. "Sweet" defines a petroleum as having little sulfur contamination: South Louisiana crude is about 84% carbon and 4% hydrogen, and often less than one per cent sulfur by weight. Minor amounts of heavy metals (on the order of 11 ppm vanadium and 8 ppm nickel) may also be bound within heterocyclic structures (American Petroleum Institute 2003).

Spilled crude usually floats to the surface because it is less dense than sea water. Clearly, this is occurring with the DH material: more than 10 million feet of containment and sorbent boom have been used to control the surface oil and more than 600 miles of shoreline have been oiled (JIC-DHUC[1], Administration Response, August 8, 2010 update). Based on the National Incident Command Oil Budget report of August 4, 2010, at least 8% of the oil released prior to capping reached the surface. This amount is documented to have been burned or skimmed (U.S. Dep't of the Interior 2010). Surface oil appears to be taking forms similar to those experienced during other petroleum spills: oil slicks and sheens, mousse (water-oil emulsions), and tar balls (sticky, petroleum-derived material with a weathered surface). The oil that escaped from the DH well hole was under great pressure (8000-9000 PSI, as reported by BP) and contained a significant proportion of natural gas, primarily methane. This methane accumulation contributed to the drilling platform explosion, and is responsible for the dramatic, continued expulsion of petroleum at the failed well. The way in which the oil was released was compared to the ejection of liquid from an aerosol can, and the group speculated that this, together with the injection of dispersants at the well-head (more below), contributed to the formation of extremely small droplets. These micro-droplets measure about a millionth of an inch in diameter. Micro-droplets do not float to the surface and have been found in deep-water plumes at approximately 2,300 to 4,200 feet depth (M. Joye pers. comm.) It is not clear how long these droplets will persist, particularly in the cold temperatures of deep Gulf waters.

b. Methane Gas

The DH oil contains approximately 40% methane (by weight) compared to the usual 5% (Kessler 2010). In addition to its effects on the discharge of oil, the transport and reactivity of the methane itself is also of concern. At typical sea-surface atmospheric pressure, methane is a volatile gas. However, at the depth (5,000 feet) and low temperature (approximately 41°F) of the leak site, methane forms a hydrocarbon ice called a hydrate. Hydrates can also form higher order "cage" structures, called clathrates, which can entrain other alkanes. Once they rise to a depth of about 4,200 feet, hydrates melt, at which point the methane goes into solution. In some areas near the failed well, seawater concentrations of methane have been measured at levels up to a million times background (Kessler 2010).

c. Dispersants

Dispersants are used to break up liquid hydrocarbons into microscopic droplets, thereby breaking up large slicks into smaller patches and droplets. They are commonly applied to oil once it reaches the surface, but they can also be used below the surface. One of the working groups at the recent Deepwater Horizon Dispersant Use Meeting reported ten benefits of subsurface dispersant application including: reduction in the emulsified oil at the surface, reduction in

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[1] JIC-DHUC: Joint Information Center - Deepwater Horizon Unified Command

volatile compounds at the surface (a personnel safety issue during cleanup operations), reduction of phototoxic impacts (the process where sunlight converts some forms of oil into toxic compounds), and accelerated microbial degradation (Coastal Response Research Center 2010).

1.84 million gallons of dispersant were used in the Gulf of Mexico to address the DH leak. Of this, the majority (>1 million gallons) was applied at the surface (JIC-DHUC 2010). Fluorescence studies suggest that oil in the top 30 feet is being affected by surface application of dispersant (Coastal Response Research Center 2010). As described above, the deep-water oil plumes that have been observed in the Gulf of Mexico are thought to be comprised of micro-particles released under great pressure from the well site. The large *deep-sea* application of dispersant is unprecedented. It is likely that the under water application of dispersant has greatly contributed to the formation of micro-droplets, as the dispersant also acts to stabilize particles or droplets suspended in water.

Two different dispersants (Corexit® EC9527A and Corexit® 9500A, both manufactured by Nalco Company) were used on the DH material. The two formulations are similar: both contain an organic sulfonic acid salt[2], solvents, and emulsifiers. Corexit® EC9527A contains a solvent of concern for both human and ecological health (2-butoxyethanol). In Corexit® 9500A (a later formulation), the 2-butoxyethanol has been replaced by light petroleum distillates (see below).

Corexit® EC9527A is the dispersant used early after the well failure. The Material Safety Data Sheet (MSDS) identifies it as a clear, amber liquid, soluble in water and lists the percentage of hazardous substances as recorded below. The function of each substance is also included.

Corexit® EC9527A

Hazardous Substance(s)	CAS NO	% (w/w)	Function
2-Butoxyethanol	111-76-2	30.0 - 60.0	Solvent (carrier)
Organic sulfonic acid salt	Proprietary	10.0 - 30.0	Anionic detergent
Propylene Glycol (also called 1,2-Propandiol)	57-55-6	1.0 - 5.0	Solvent (emulsifier)

Corexit® EC9500A is the dispersant used later in the process and in the larger quantity. The MSDS identifies it as a clear hazy, amber liquid, miscible in water and lists the percentage of hazardous substances as recorded below.

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[2] The sulfonic acid detergent component has been identified on the U.S. EPA website as the sodium salt of butandioic acid, 2-sulfo-, 1,4-bis(2-ethylhexyl) ester , CAS registry number 577-11-7 (U.S. EPA 2010).

Corexit® EC9500A

Hazardous Substance(s)	CAS NO	% (w/w) (from MSDS)	Function
Distillates, petroleum, hydrotreated light	64742-47-8	10.0 - 30.0	Solvent (carrier)
Organic sulfonic acid salt	Proprietary	10.0 - 30.0	Anionic detergent
Propylene Glycol (also called 1,2-Propandiol)	57-55-6	1.0 - 5.0	Solvent (emulsifier)

The mixture works to disperse droplets of oil by surrounding them with detergent molecules. This is an anionic detergent: each molecule has hydrophobic portions that associate with oil, and hydrophilic portions that associate with water. Three sorbitan derivatives and two other solvents are also listed by the U.S. EPA as components of the dispersant mixture.

Oil from another historical Gulf of Mexico spill, the Ixtoc 1 exploratory well explosion (under the Bay of Campeche, June 3rd, 1979), was also treated extensively with dispersants. One resource claims that 2.5 million gallons of dispersant were used at the surface, at least some of which was Corexit 9527, later renamed Corexit® EC9527A (Coastal Response Research Center 2010).

II) Processes that Affect DH Material

Human cleanup efforts and natural degradation and weathering processes are working to reduce the total amount of DH material in the Gulf of Mexico. The longer oil remains in the Gulf of Mexico, the less it will resemble the material that leaked from the failed well. Below we briefly describe each of the processes that could serve to transform DH material before (or during) transport to the East Coast. We then describe the conclusions of the panel with respect to this issue.

a) **Human Intervention**

   i) Direct Removal The oil budget team reports that as of August 4, 2010 approximately 800,000 barrels of oil were recovered through direct capture from the wellhead (U.S. Dep't of Interior 2010). The team also reported that some 165,000 barrels were removed from surface waters by skimmers and the use of absorbent booms and more than 265,000 barrels were removed through on-site, controlled burns (U.S. Geological Survey 2010).

   ii) Chemical Dispersal Although their use is somewhat controversial, chemical dispersants have been and continue to be used to alter the nature and fate of spilled oil. As described above, dispersants coat individual droplets of oil and can thus help break up oil slicks and other patches. Dispersed oil is not as sticky and is therefore

less likely to coat birds and mammals. Dispersed particles can also be more susceptible to weathering and microbial degradation (see below).

b) Natural Processes (Weathering)

Weathering is a collective term for a number of interrelated, natural processes that affect the form and chemical composition of hydrocarbons in the environment (Figure 1), each of which is briefly described below. The physical form of the oil can make it more or less susceptible to these transformations. If oil has been broken into smaller particles, either through natural processes or the application of dispersant, the particles' increased surface area to volume ratios makes more of the oil accessible to weathering processes. The location of the oil will also affect processing. For example, the increased pressure and lower temperature at depth may affect both the physical properties of the oil and the type and activity of oil-degrading microbes.
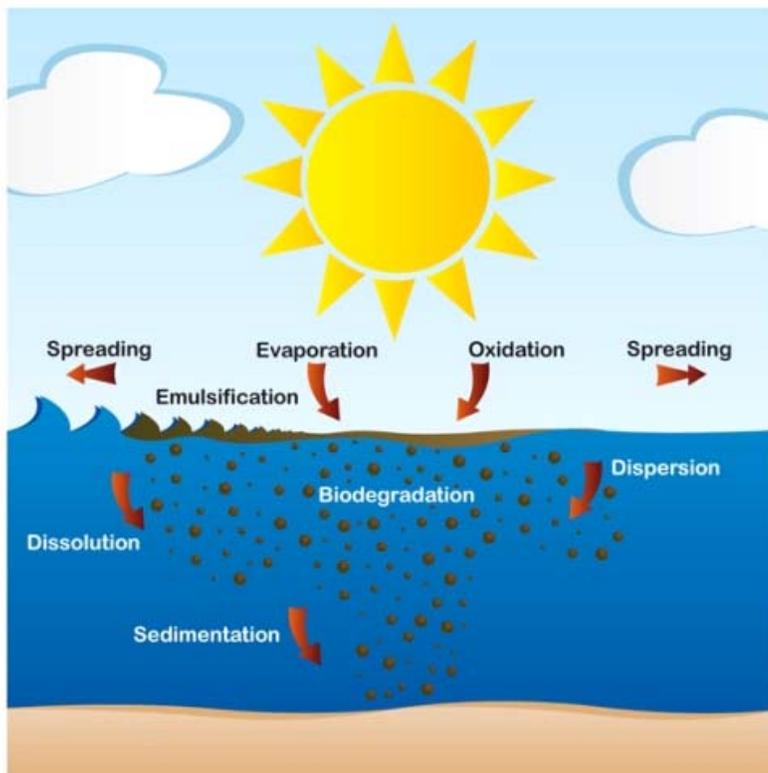

Figure 1. Weathering processes that affect oil. Source: http://www.itopf.com/marine-spills/fate/weathering-process/

    i)   Spreading and Dispersion of surface oil is caused by wind, waves, currents, storm action, and the activity of vessel operations in the area. This type of spreading is not uniform, so it is common to see variations in the thickness of the oil layer. Once dispersed, material often undergoes additional chemical weathering processes.

ii) <u>Evaporation</u> (also called <u>volatilization</u>) takes place in surface waters when short chain (usually restricted to compounds with fewer than ten carbons) or small aromatic hydrocarbons transfer into a gaseous phase such as air. Unfortunately, this process may affect air quality. Evaporation is a significant weathering process: "In many spills, evaporation is the most important process in terms of mass balance. Within a few days of a spill, light crude oils can lose up to 75 percent of their initial volume" (National Research Council 2003, p90). The spreading of surface oil through wind and wave action will increase evaporation. This is a temperature dependent process, so one might expect that high air and water temperatures in the Gulf of Mexico in late spring and summer would result in high rates of surface oil evaporation. However, the government estimates for the DH spill evaporation (through August 1, 2010) is only about 25 percent (U.S. Geological Survey 2010). Another recent study reports that alkanes up to C14 are volatilizing (Coastal Response Research Center 2010). The best explanation for these observations is that the portion of oil reaching the surface is volatilizing rapidly, but that much of the oil remains in subsurface forms.

iii) <u>Photo-oxidation</u> is the chemical transformation of molecules by light energy. Like evaporation, this is also a process that occurs only at the ocean surface. Large crude oil hydrocarbons (especially the PAHs) absorb solar radiation and are directly transformed by photolysis[3]. Some products are highly polar, which enhances their solubility and concomitant microbial degradation (see below). Others are volatile compounds that can evaporate. Whereas microbial degradation and evaporation serve to reduce the amount of petroleum hydrocarbon in the water column, photo-oxidized oil can also polymerize and form persistent tars and emulsions. Finally, photo-oxidation can transform oil species (particularly PAHs) into toxic molecules. Photo-ionization can also occur in the spill or in cells of organisms after target hydrocarbons bioaccumulate. For example, photo-ionization of PAH-derived molecules bound to DNA can form nucleotide-damaging free radicals in bacterial cells. Photo-toxicity can have both acute and chronic effects on various near-surface organisms (Lee 2003).

iv) <u>Emulsification</u> of seawater and oil can occur in surface waters under turbulent conditions. Water is integrally mixed into the oil, increasing the volume of the hydrocarbon mixture, and giving it a mousse-like appearance. Oils high in asphaltenes are particularly prone to creating these relatively long-lived emulsions

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[3] Compounds resulting from photo-oxidation of petroleum (reviewed by Lee, 2003) include: "aliphatic and aromatic ketones, aldehydes, carboxylic acids, fatty acids, esters, epoxides, sulfoxides, sulfones, phenols, anhydrides, quinones and aliphatic and aromatic alcohols."

(ITOPF and Lee 2003). Fortunately South Louisiana crude generally has a very low asphaltene content. In a related process called flocculation, a well-mixed, fluid colloid of oil and water can shed flakes of particulate, insoluble material. These changes in physical form will affect how accessible the oil is for other types of weathering.

v) <u>Dissolution</u> of the water-soluble components of petroleum mixtures (such as benzene and toluene) does occur, and may be an important process in the removal of the soluble fraction of subsurface oil. Physical mixing of the contaminated water will result in some portion reaching the surface. At this point, volatile molecules are readily lost through evaporation.

vi) <u>Biodegradation</u> of oil takes place when bacteria utilize petroleum as a source of carbon and energy. The process is dependent on temperature, nutrient and oxygen availability, as well as the physical and chemical form of the hydrocarbon substrate. Although the microbial community is well adapted to utilizing carbon from natural seeps in the Gulf of Mexico, some hydrocarbons are more accessible (physically and biochemically) than others. A study of different hydrocarbon substrates found that n-paraffins are utilized preferentially over the aromatics or napthenes (Aldrett 1997). The amount of paraffins in South Louisiana crude is reported at 79% by volume (American Petroleum Institute 2003), which suggests they should be readily consumed by bacteria. Indeed, studies of the DH surface slicks have shown that clusters of bacteria form in as little as 24 hours and after another day, bacteria and oil can be visualized as filaments on the surface (M. Joye, pers. comm.). Methanotrophic bacteria (which consume methane) can also utilize the methane in subsurface plumes: M. Joye has measured methane oxidation rates in a subsurface plume at 1-5% per day, which is orders of magnitude higher than normal (pers. comm.). These high levels of activity should result in less toxic material available for transport throughout the Gulf of Mexico and to the Atlantic.

vii) <u>Sedimentation</u> of heavily weathered (tar-like) oil occurs when the oil adheres to particles of sand, shell, rock, or coral and it is then transported with the particle. Tars can also adhere to, or be entrained in *Sargassum*, wrack, debris, or other matrices - each with different effects on buoyancy. If such masses wash up on beaches and are buried, weathering slows.

c) Conclusions

All of these pathways are likely occurring, serving to transform DH crude oil. By way of comparison, it is informative to evaluate the fate of the oil in the Ixtoc 1 leak in 1979 (where chemical dispersant was also used [U.S. Department of Commerce 1981]). An estimated 6% of

the oil was removed from the spill site by burning and booming, approximately half of it evaporated, 12% was transformed via photo oxidation and microbial transformation, and 25% of it flocculated and sank (where microbial activity presumably continued). Only 7% of the oil was estimated to make landfall. The most long-lived component of the material is reported to be aromatic compounds, which have been detected quite far from the spill site. Tar balls were a common feature on South Florida beaches for many years following the spill.

It is difficult to know how much of the material in the Gulf of Mexico will reach the East Coast, but the longer it stays out of the Loop Current, the more time there will be for weathering processes to occur, so the expectation is that both the concentrations and toxicity of any oil that reaches the Southeast will be substantially lower than at the DH site. If the Ixtoc spill is an appropriate analogy, then we can expect evaporation and sedimentation to be the dominant weathering processes. However, the deep subsurface plumes of microscopic droplets of oil (with or without dispersant) are unlike any known historic oil spill and it is not known how long they will persist. However, the known subsurface plumes are considerably deeper than the Loop Current so this material is less likely to be transported to the east coast unless it is first mixed to shallower depths. The panel concluded that the most likely forms of material that will reach the Southeast would be persistent emulsions, subsurface micro-droplets and highly weathered tar balls.

III. Recommendations

The group discussed a variety of activities that would enable us to inform decision-makers and response teams of the presence of various forms of oil throughout the Southeast region. Components of a coordinated monitoring and research program could include:

- *Fluorescence sensors* could be deployed in the Florida Current to serve as an initial sentinel for the detection of oil in the water column. The more weathered the oil, the more fluorescence we can expect. However, concentrations are likely to be low and instruments should be optimized to measure oil fluorescence signatures to improve the likelihood of detection. This method will not detect solid forms such as tar balls and tar mats.
- *Tar ball counts* and surveys could be done by volunteer groups on regional beaches as well as by ships performing local survey work (fisheries and otherwise). Surface tar ball abundance estimates have been performed in the past using neuston net tows (Cordes et al. 1980) and such estimates could provide estimates of both the background and DH-generated abundance of such pollutants. The information could be organized in a GIS

database with temporal data layers. A synergistic activity would be to record the presence of flotsam and plastics (with and without visible contamination).

- *Water sampling* could be performed in the Gulf Stream along the length of the South Atlantic Bight. These samples would be solvent extracted (e.g. with dichloromethane) to look for a fluorescence signature and hydrocarbon fingerprinting via gas chromatography-mass spectrometry (see below). One could also use monoclonal antibody kits for the detection of certain PAHs in water samples. Water samples could also be tested for microbial indicators as an "echo" of oil. A baseline should be established soon.

- *Sentinel organisms* that have high rates of water filtration and would naturally concentrate oil (e.g., copepods and sponges) could be targeted for analysis. Those samples may fluoresce in situ or could be similarly solvent extracted for fluorescence measurements.

- *Satellite remote sensing* could be used to detect oil accumulations at the sea surface. It may be possible to screen for 3-4-5 ring aromatics in clear water across the shelf. Modeling and monitoring of loop-current-spill interactions could help guide some of the imagery acquisition priorities. An alternative approach would be to employ sheen refraction: oil has effects on sheen which can be visualized by altering the angle of observation. Capillary waves are smoothed by petroleum at the surface, so sea-surface topography can also be a useful detection method.

- *Gliders* equipped with synchronous fluorescence scanning capability (or EEMS excitation emissions) could be used to provide synoptic information on the distribution of oil across the shelf, especially if other indications predict the transport of oil into the Gulf Stream.

- *Fingerprinting* Since the background (non-DH) hydrocarbon seepage in the Gulf of Mexico is significant[4], methods are needed to distinguish chronic oil contamination from that associated with the DH event. Hopanes and steranes are relatively stable components of petroleum mixtures which can be used as a source fingerprint. Analysis of compound-specific hydrogen or carbon isotopic signals may also be useful. Obtaining compositional information (directly or through collaboration with Gulf Coast groups) on the DH spill is critical. A number of techniques previously used to discriminate between Ixtoc 1 well oil and that from a concurrent shipping accident may be useful during the DH response (ERCO 1982).

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[4] estimated at more than 40 million gallons per year (NRC 2003)

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Appendix A: List of Participants

Technical Experts:

Michael Aitken, Professor and Chair, Department of Environmental Sciences and Engineering, University of North Carolina – Chapel Hill, mike_aitken@unc.edu
Research interests encompass the application of microbial processes to the biodegradation of organic pollutants (particularly polycyclic aromatic hydrocarbons); the use of cultivation-independent molecular tools to identify and quantify microorganisms capable of degrading specific chemicals in complex systems; and how bioavailability governs the rate and extent of degradation of hydrophobic chemicals in contaminated systems.

Jay Brandes, Associate Professor, Skidaway Institute of Oceanography, jay.brandes@skio.usg.edu
Research interests include the use of stable isotopes to determine the source and diagenesis of organic compounds and nutrients in marine ecosystems. Developing high resolution X-ray spectromicroscopic techniques to examine nutrient cycling and sequestration and organic matter diagenesis.

Samantha (Mandy) Joye, Professor, University of Georgia, mjoye@uga.edu
Research interests include biogeochemical cycling of nutrients, metals, and organic materials in coastal environments; biogeochemistry of methane hydrate and chemosynthetic habitats; ecosystem and geochemical modeling; microbial ecology, metabolism and physiology; molecular biology; global nitrogen cycle, global methane cycle.

Richard (Dick) Lee, Professor, Skidaway Institute of Oceanography, dick.lee@skio.usg.edu
Research interests include chemical oceanography, contaminant source, fate, effects. Currents projects on DNA damage and embryo development in grass shrimp exposed to contaminants, blue crab disease in Georgia, and mariculture of black sea bass for the sushi market.

Ralph Mead, Assistant Professor, Department of Chemistry and Biochemistry, University of North Carolina – Wilmington, meadr@uncw.edu
Research interests are in the field of marine organic geochemistry with emphasis of tracing naturally-derived organic carbon; carbon cycling in estuarine systems; bulk and compound specific stable carbon isotopic analysis to elucidate the source and cycling of organic mater within the marine environment; and organic-mineral interactions.

William (Bill) Miller, Professor, Marine Sciences Department, University of Georgia, bmiller@uga.edu
Research interests include photochemical reactions and their effect on aquatic carbon cycles; distribution of trace carbon gases; alteration of aquatic humic substances; and relation to optics and biological processes.

Andrew Ogram, Professor, Soil and Water Science Department, University of Florida, aogram@ufl.edu
Research interests include analysis of pollutants on wetland biogeochemical processes and biological degradation of organic compounds in soils. Previous work has included development and validation of molecular indicators of microbial communities to fuel oil contamination.

Geoff Scott, Director, Center for Coastal Environmental Health and Biomolecular Research, Charleston, South Carolina, National Centers of Coastal Ocean Science, National Ocean Service, NOAA, Geoff.scott@noaa.gov
Dr. Scott holds adjunct faculty appointments at the Medical University of South Carolina, University of South Carolina, University of Charleston, and Texas Technical University. Research experience includes studies of the nature and relationship of oil and hazardous material spills within coastal ecosystems through the U.S. including studies in Alaska, Puget South, Texas, Puerto Rico and the Florida Keys.

Ming-yi Sun, Professor, Marine Sciences Department, University of Georgia, mysun@uga.edu
Research interests include biogeochemical cycling of organic matter in estuarine and coastal marine systems. Influence of global climate change on Arctic benthic ecosystems. Effects of diagenetic processes on biomarker compositions and compound-specific stable carbon isotopic compositions. Interactions between organic compounds and biota.

Eric Triplett, Professor and Chair, Department of Microbiology and Cell Science, University of Florida, ewt@ufl.edu
Research focus is on the drivers of microbial diversity in a wide variety of environments. Investigating which bacteria and archaea are associated with the presence of oil in the Gulf of Mexico.

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