2015 Gulf of Mexico Oil Spill & Ecosystem Science Conference

Abstracts of Oral Presentations

Session 001
Data Management and Informatics Supporting Ecosystem Sciences

Pulling Together Growing Data to Fuel Ecosystem Models: An Introduction to rglobi and ratlantis

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As data related to the Deepwater Horizon Oil Spill and the Gulf of Mexico continues to accumulate in the decade following the spill, there is a growing need for tools and workflows that can allow this information to be synthesized and put to use. While ecosystem models are excellent examples of systems that have the capacity to utilize a wide array of available data in predicting future impacts of the spill, they also demonstrate common issues with dealing with a data source that is constantly evolving. The development of these models is often hampered by the need to access and merge various types of data. This commonly leads to the inability to quickly update or focus models based on new information and limits their application. To address these issues, we describe a set of tools and associated workflow that facilitate the discovery of data from multiple sources and expedite the integration of data into ecosystem models. Currently in development on github, rglobi pulls data on species interactions from the Global Biotic Interactions database, which includes the GoMexSI database. ratlantis offers an R-based interface to the Atlantis ecosystem model source code that employs rglobi and other packages to quickly create and update ecosystem models. These tools automate much of the model development process and offer a new workflow for creating and comparing ecosystem models. I demonstrate the application of this process in developing a new Atlantis model for the eastern Gulf of Mexico. These tools also demonstrate how open science applications and collaborative technologies such as github offer paths to dealing with growing data sources and their implications.

Gulf of Mexico Species Interactions (GoMexSI): Building a Baseline Database of Gulf-wide Species Interaction Networks for Perturbation Response Models

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Many fishery ecosystem models have been created in the Gulf of Mexico. One significant commonality is their reliance on diet data for species or functional groups being modeled. For a new model, diet data must either be searched for, or use a modified diet matrix used by a previous model. Time constraints usually prevent one from examining all data available for the system of interest. We report on the Gulf of Mexico Species Interaction (GoMexSI) database, built on Neo4j technology, and webpage (gomexsi.tamucc.edu), that can streamline the process of diet data acquisition for future Gulf ecosystem models. While the database aims to include all types of species interactions, we are currently focused on predator-prey interactions of fishes. The database is constructed by extracting species interaction data

from historical references and user-contributed datasets, and is managed using Github. Currently the database includes 37,930 interactions from 61 references/contributors, representing 1,346 unique interactors. Users can query data and view summaries online, or they can download raw data downloaded to a csv file. There are also pages for spatial query tools and exploration of predator and prey webs for specific species. We are examining diet data shortfalls through taxonomic and spatial gap analyses and adding new data through stomach content analyses. Many of these data are being targeted for a Gulf-wide Atlantis model, and will be useful for other ecosystem models under development.

Cryptographic Hashing of Research Data Files to Ensure Data Integrity

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Today, most scientific research data is recorded in electronic format, which not only facilitates analysis, but also data sharing. To facilitate data sharing, there exist a number of repositories for electronic scientific data, such as the National Oceanographic Data Center (NODC), Dryad, and the Gulf of Mexico Research Initiative Information and Data Cooperative (GRIIDC). An important issue data providers, data consumers, and the repositories themselves face is how to ensure integrity of the electronic data as it is passed from the provider, to the repository (and within the repository), and ultimately to the consumer. The assurance of data integrity is important, not only for scientific, but also for legal reasons, especially in oil spill-related research, where findings could have an economic and/or legal impact. Cryptographic hashing is a common method used to ensure the contents of electronic files have not been altered in any way. This talk will discuss using cryptographic hashing as a means of ensuring data integrity, along with novel methods for generating these hashes efficiently for large data files using freely available tools. It will also discuss methods of recording these hashes in common metadata formats (such as ISO 19115-2) and using them as a part of or even as a possible alternative to the Digital Object Identifier (DOI) System.

Enabling Near-Real-Time Mitigation with Web Services for Sharing Buoy Data: Potential Applications for Marine Mammal Monitoring in the Gulf of Mexico

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The Bioacoustics Research Program at the Cornell Lab of Ornithology has developed a system for near-real-time marine acoustic monitoring, enabling immediate mitigation of anthropogenic activities pursuant to environmental regulations by providing a framework for shore-side clients to assess noise and monitor animal presence. The system consists of a buoy-mounted electronics package that communicates with a shore-side server via Iridium satellite or GSM/GPRS. The server parses received reports from the buoys into a series of file assets (audio clip files and spectrogram preview images) stored on scalable storage, and metadata (date/time, score, feature vector, algorithm, GPS location, battery voltage, and other status information) inserted into a relational database. These data are then made available via Apache, PHP and Django by a number of web and data interfaces. Analysts are notified by either email or text message about detections that can be reviewed remotely using a custom web interface that includes spectrogram views, audio playback, and annotation capability. Timely information can be distributed to mariners, researchers, and others via Flash-based web interfaces (see

www.listenforwhales.org), KML/Google earth, email reports, phone calls, text messages, and AIS broadcasts. Already successfully deployed on the U.S. East Coast and in the Arctic, the system has the potential to offer near-real-time data to oil spill or seismic activity mitigation in the Gulf of Mexico.

US IOOS Data Management Services to Address Biological and Ecosystem Data Integration to Support Ecosystem Sciences in the Gulf of Mexico

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An important Data Management and Communication (DMAC) goal is to enable a multi-disciplinary view of the ocean environment by facilitating discovery and integration of data from various sources, projects and scientific domains. United States Integrated Ocean Observing System (U.S. IOOS) DMAC functional requirements are based upon guidelines for standardized data access services, data formats, metadata, controlled vocabularies, and other conventions. So far, the data integration effort has focused on geophysical U.S. IOOS core variables such as temperature, salinity, ocean currents, etc. The IOOS Biological and Ecosystem Observations Services are addressing the DMAC requirements that pertain to biological and ecosystem observations standards and interoperability applicable to U.S. IOOS and to various observing systems. Biological and ecosystem observations are highly heterogeneous and the variety of formats, logical structures, and sampling methods create significant challenges. Here we describe an informatics framework for biological observing data that is already expanding information content and reconciling standards for the representation and integration of these biological observations for users to maximize the value of these observing data. We further demonstrate an initial implementation in the Gulf of Mexico Ocean Observing System Regional Associations (GCOOS-RAs) and Southeast Coastal Ocean Observing Regional Association (SECOORA) with existing Federal and state biological data. We then recommend to employ data definition conventions that are well understood in U.S. IOOS and to combine these with ratified terminologies, policies and guidelines.

Metadata Lessons Learned for Highly Varied Data Collections

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The Gulf of Mexico Research Initiative Information and Data Cooperative (GRIIDC) is charged with storing, managing, and distributing the research data developed from projects funded by the Gulf of Mexico Research Initiative (GoMRI). For these data to be most useful to future researchers, data documentation, or metadata, is essential. Additionally, GRIIDC relies upon metadata for a number of functions including data discoverability, system planning and scheduling, and reporting throughout the data lifecycle. The data generated by these projects are highly varied, in discipline, scale, and size, and as a result GRIIDC faces serious challenges. The varied nature of the data and different community practices make standardization difficult and metadata generation onerous. This presentation will discuss the progress and lessons learned for the GRIIDC metadata program to date, including measurements of metadata quality, evaluation of the metadata submission and review processes, and upcoming improvements to address identified problem areas.

Going Beyond the Publication: NETL's Energy Data Exchange (EDX) - A Coordination and Collaboration Platform to Help Make Science More Accessible

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A common problem faced by researchers, particularly in relation to long-term, interdisciplinary, "big" data projects, is how to make the lessons learned as well as the data, data-derived products, and tools, more widely available to help improve academic, research, public, and policy understanding. With numerous projects focusing on offshore energy resources to develop a scientific base for reducing and quantifying potential risks associated with exploration and production in offshore environments, NETL has developed the Energy Data Exchange (EDX) to address the issues of finding pertinent, relative datasets, sharing data, and developing projects across multi-organizational teams. EDX serves as an online coordination and collaboration platform, providing capabilities to better facilitate research, improve knowledge transfer and data discovery, as well as provide broad access to key data, products, tools and results. For this presentation, we'll focus on EDX's data sharing, use, and citation policies, the platform's workflow, integration capabilities with other web services and portals, and future plans for the platform over the next decade.

Open Standards-based Data and Information Sharing to Enhance Environmental Science

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Information sharing is common today in social media; almost ubiquitous when considering websites like Facebook. However, in the science community, a number of social, political and economic determinants often favor withholding information rather than sharing it. For example, critically important results or a disruptive discovery, that by their nature should be peer reviewed, mandates at least a delay in sharing of raw data or resultant information.

It is crucial to explore how to avoid underutilization of data and unavailability of valuable scientific conclusion; specifically for scientific output that is needed for good policy making, effective industrial practices, and meaningful environmental stewardship. A standards-based information sharing platform, including rich information management tools, is needed as a foundational element in the broad scientific efforts ongoing in the Gulf of Mexico. Such a platform, along with the tool set, would provide learners, scientists, program managers, and policy makers the information they need. Further, the information produced from such a platform will substantially increase efficiency in application of limited fiscal resources, i.e. through promotion of collaboration, identification of critical scientific needs, and more. Presented is a summary of a recently developed open-standards-based information sharing platform, relevant information management tools, and example applications in Gulf of Mexico environmental science.

Managing and Accessing Natural Resource Damage Assessment Data from the Deepwater Horizon Oil Spill

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The Deepwater Horizon oil spill in the Gulf of Mexico in 2010 and the ongoing Natural Resource Damage Assessment have generated unprecedented amounts of environmental data and analysis. As a trustee for Natural Resources, NOAA's Office of Response and Restoration faced the challenge of managing and integrating many datasets from numerous separate collection systems with varying levels of organization and documentation. Our team addressed this challenge by leveraging "big data" techniques and developing a data warehouse and information portal built with Open Source tools for ingesting, integrating and organizing information. We have organized data holdings into "common data models", and directly connect field collected information with laboratory results and supporting information. We further developed custom query tools which facilitate querying across all data holdings or focusing on specific results. This novel data management and query approach is called DIVER (Data Integration, Visualization, Exploration, and Reporting), and forms the primary portal for data mining and sharing across Trustees and with Responsible Parties. The data query tools within DIVER allow users to explore the environmental datasets based upon a common core set of data fields plus specialized fields applicable to specific data types (e.g., Analysis Types.). Users can choose query templates or start from scratch to quickly obtain data, analysis, and results and also save queries. Once the search is performed, users are presented with an interactive map displaying the results, interactive charting and table for data exploration, and data export. Data export packages include detailed FGDC metadata, field definitions, and data caveats.

Advancing a Data Sharing Culture

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Even though there is conceptual agreement in the scientific community that freely sharing data leads to greater understanding, there remain impediments to accomplishing this goal. These impediments include lack of motivating reasons for researchers to share, the cost of sharing to researchers, the lack of training and support for how to share, and in some disciplines, the lack of technical resources, such as data repositories, through which to effectively share data. To develop a culture of sharing, a variety of motivations to individuals need to be provided, and the Gulf of Mexico Research Initiative (GoMRI) is taking the following approaches: creating a data management system that is simple to use and robust for submitting and discovering a variety of data; providing one-on-one assistance during the submission process; providing metadata tools and a review service for documenting datasets; and providing DOIs and feedback to researchers on data downloads. Furthermore, GoMRI has a strict requirement and enforcement for data management and making data publicly available during the course of research projects. The community should apply other strategies to advance data sharing including requirements by publishers to have data, on which scientific papers are based, openly available, consideration by universities of shared datasets in promotion reviews, and funding programs to require realistic budgets and plans for data management as well as evidence for past data sharing.

Preparing Data Management Systems for the Next Environmental Disaster

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In the wake of the Deepwater Horizon disaster, a flood of data and new research highlighted the need for improved coordination of data management for environmental applications. It is common for multiple entities (NGOs, academic institutions, federal and state agencies) to collect data for an incident that vary significantly in characteristics such as, data quality objectives, collection methods, and access. These differences in data management result in limitations for use of the data including comparing results or making inferences. This presentation will discuss the results and actions from a workshop on "Environmental Disaster Data Management." This effort sought to foster communication among data collectors, managers and users within the scientific and research communities, industry, NGOs, and federal and state agencies, with a goal to identify and establish best practices for orderly collection, storage and retrieval. Participants discussed and prioritized needs in the areas of common data models, best practice for reducing errors from collection to dissemination, infrastructure requirements, data visualization, discovery and delivery methods, and actions for moving toward better methods for sharing data across organizations.

Session 002
Oil-Dispersants-Sediment Interactions and Weathering/Degradation of Spilled Oil in Gulf of Mexico Ecosystems

Molecular-level Identification of Metal-Containing Compounds from Oil Contamination Released from Natural Seeps and Anthropogenic Spills

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Although natural petroleum seeps to the ocean account for nearly half of all input, only a small number of seafloor features associated with active seepage have been characterized. Here, we describe the detailed, molecular-level characterization of polar species and petroporphyrins accessible only by ultrahigh resolution FT-ICR mass spectrometry. Recent advances in chromatographic fractionation and instrumentation conditions provide unprecedented insight into the structural diversity of petroporphyrins at the molecular level. Here, we employ offline liquid chromatography combined with Fourier transform ion cyclotron resonance (FT-ICR) MS and MS/MS to identify structural cores unique to petroporphyrins in weathered oil, derived from anthropogenic spills and natural seepage. Oil contamination derived from the *M/V Cosco Busan* spill (2007), Kirby cargo spill (2014), and Deepwater Horizon spill (2010) will be compared to natural seepage from the Gulf of Mexico (GC 600) and Santa Barbara basin. Work supported by the National Science Foundation through DMR-1157490 and the BP/Gulf of Mexico research Initiative to the Deep-C Consortium.

Effects of Oil Dispersant on Photodegradation of PAHs in Seawater

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The effects of Corexit EC9500A on the photochemical degradation of PAHs (pyrene, anthracene, 9,10-dimethylanthracene) were tested with simulated sunlight in seawater. The results showed that Corexit EC9500A enhanced photodegradation of all the PAHs, and the photodegradation rates showed a two-stage kinetics, each following the first-order rate law. GC/MS analyses suggested the dispersant does not alter the photodegradation pathway for the PAHs though the dispersant was degraded concurrently. The presence of the dispersant components (Span 80 and kerosene) resulted in an elevated concentration of PAHs in the surface layer of the water column, which favors the photodegradation. Dissolved oxygen (DO) played an important role in the photodegradation process, and the presence of Corexit EC9500A greatly leveraged the role of DO. Both 1O2 and O2•- radicals played important roles in the absence of the dispersant. However, the presence of the dispersant inhibited the contribution of 1O2 but enhanced the role of O2•-, which was nearly 100% responsible for photodegradation process. The results may aid in understanding the roles of dispersants on environmental weathering of spilled oil and persistent oil components.

Effects of Oil Dispersants on Formation of Marine Oil Snow and Related Transport of Oil Hydrocarbons

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This work explored the formation mechanism of marine oil snow (MOS) and the associated transport of oil hydrocarbons in the presence of a stereotype oil dispersant, Corexit EC9500A. Roller table experiments were carried out to simulate natural marine processes that lead to formation of marine snow. We found that both oil and the dispersant greatly promoted the formation of MOS, and MOS flocs as large as 1.6-2.1 mm (mean diameter) were developed within 3-6 d. Natural suspended solids and indigenous microorganisms play critical roles in the MOS formation. The addition of oil and the dispersant greatly enhanced the bacterial growth and extracellular polymeric substance (EPS) content, resulting in increased flocculation and formation of MOS. The dispersant not only enhanced dissolution of n-alkanes (C9-C40) from oil slicks into the aqueous phase, but facilitated sorption of more oil components onto MOS. The incorporation of oil droplets in MOS resulted in a two-way (rising and sinking) transport of the MOS particles. More lower-molecular-weight (LMW) n-alkanes (C9-C18) were partitioned in MOS than in the aqueous phase in the presence of the dispersant. The information can aid in our understanding of dispersant effects on MOS formation and oil transport following an oil spill event.

Laboratory Tests of Biochars as Absorbents for Use in Recovery or Containment of Marine Crude Oil Spills

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Economical means of rapidly responding to oil spills at sea are needed. The use of high-capacity absorbents is one approach. Biochar is the carbonaceous byproduct of anoxic pyrolysis of biomass wastes. It is a porous and hydrophobic material. The absorption capacity of different biochars for crude oil, and the mineralization potential of the absorbed oil in seawater were determined in laboratory experiments. Texas, South Louisiana, or Qua-Iboe Nigeria crude oils were contacted with each of four commercial hardwood biochars and six synthesized wood biochars (300 to 700 oC, 2 h) in seawater from the Gulf of Mexico and Long Island Sound (U.S.). The oil absorption capacity of the biochars determined in dip tests using oil on seawater ranged from 3.6 to 6.3 g/g. The oil-imbibed biochar particles are buoyant. Seawater enhanced absorption capacity in relation to the H/C ratio. Oil was less effectively absorbed in the form of weathered water-in-oil microemulsion ('mousse') than in as-received form. Absorption capacity peaked at HTT about 400 oC and correlated poorly with % C, H/C ratio, O/C ratio, surface area, or porosity. It is proposed that swelling, in addition to macropore filling, may enhance absorption. In biometer tests, CO2 evolution from sub-capacity levels of Texas crude absorbed in biochar and suspended in seawater was stimulated relative to oil in the absence of biochar. Thus, biochar may prime biodegradation by providing a favorable solid support combined with an interstitial reservoir of hydrocarbons for degrader biofilms. While less absorptive than many experimental high-tech absorbents, biochar may provide an inexpensive alternative for recovery of marine oil spills in a form suitable as a fuel or as an aid to natural attenuation.

Atmospheric Transport of Oil and Dispersants from the Air-Water Interface

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Dispersants are useful in combating off-shore oil spills. Nevertheless, there is debate regarding the transport of both oil and dispersants into different environmental sections including air, water, sediment, and biota. Dispersants consist of a mixture of solvents and surfactants. We examined the extent of the effect of surfactants on the aerosolization of oil/dispersant matter into the atmosphere by bursting bubbles. These bursting bubbles are produced in a laboratory aerosolization reactor. Our results show that different surfactants have various effects in ejection of organic matter into the atmosphere and also the dispersion of oil inside the reactor. This talk will summarize some of the current information and its implications in the general environment. These observations can help us to have a better understanding about the oil and surfactant interaction at the air-water interface and to implement possible corrections to the current dispersant formulation.

The Oxidation of Macondo Well Oil: An Update and Vision

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Numerous studies following the Deepwater Horizon disaster have identified a pool of oxidized hydrocarbons in samples from surface slicks collected while the oil was still leaking from the Macondo well in 2010 to oiled-soaked sands found on Gulf beaches in 2014. Based on initial work on these products, it was shown that they were not present in the original Macondo well oil and hence not preferentially enriched while other last less stable compounds were weathered. Rather, sample extracts have increasing amounts of bulk oxygen as Macondo well oil weathers. Follow-up studies using a wide range of wet chemical, chromatographic, and mass spectroscopic techniques have confirmed their existence and that they simply are not alkanes oxidized to 1-alcohols or acids. The unprecedented nature of this weathering sheds new light on the fate of spilled oil in the environment but also opens new lines of discussion, for example, on the processes that lead to these products, exact structures, fate and transport, bioactivity, and whether such products are formed after other spills across the globe. This talk will present an overview on what is known about the production of oxidized hydrocarbons and provide a vision for future studies.

Photochemical Changes in Water Accommodated Fractions of MC252 and Surrogate Oil Created During Solar Exposure as determined by FT-ICRMS

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To determine the effects of photochemical weathering of petroleum, surrogate and Macondo MC 252 crude oils were exposed to solar radiation during the formation of Water Accommodated Fractions (WAF) in sterile seawater. Samples were incubated in either unfiltered sunlight, with ultraviolet radiation blocked (Photosynthetically Active Radiation [PAR] only), or in darkness in a temperature controlled water bath. WAFs were collected after one and six days of exposure. Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICRMS) analysis of acidic species formed in WAFs during exposure to sunlight were compared for the different treatments. MC 252 showed formation of O4-O8, N1Ox and S1Ox heteroatom classes over 6 days of exposure to full sunlight. Surrogate oil had a very different profile where lower Ox and S1Ox species were present at day 1 and N1, N1Ox and S1Ox species persisting at day 6. Day 1 PAR exposed surrogate oil WAF showed fewer oxidation products (O3 and O4 classes) compared to MC252. By day 6, PAR surrogate exposed samples formed S1O3 and S1O4 preferentially. While photochemical differences were observed between MC252 and surrogate oils, microbial production in seawater responded similarly to both WAFs from both types of oils with the majority of the inhibition resulting from oil exposure to visible light.

Solar Production of Singlet Oxygen and Hydroxyl Radical from Thin Oil Films in the Presence of Dispersant

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Solar irradiated oil films on pure water or seawater produced singlet oxygen when irradiated. Oil was collected from the surface of the Gulf of Mexico after the Deepwater Horizon oil spill and exposed to simulated sunlight. Photochemical production of singlet oxygen was measured from thin oil films over water using furfuryl alcohol as a selective chemical probe. The loss of furfuryl alcohol and the formation of 6-hydroxy(2H)pyran-3(6H)-one were monitored. Steady state concentrations of photoproduced singlet oxygen were determined to be near 10-12 M in water under thin films of oil. Addition of dispersant (Corexit 9500A or 9527A) ranging from 1%-3% resulted in changes in the observed concentration of singlet oxygen in the aqueous phase. In addition, total singlet oxygen formation was studied using high furfuryl alcohol concentrations and varying exposure time. The total amount of singlet oxygen produced in one hour irradiations of thin oil films (100 mg, 60 microns thick) over Gulf of Mexico water and pure water were 1.9 ± 0.4 × 10-5 and 1.6 ± 0.3 × 10-5 mol, respectively. Some differences were observed when dispersant was present. Hydroxyl radical production was also measured, and aqueous concentrations of 1.2 × 10-16 to 2.4 × 10-16 M were observed for seawater and pure water under solar irradiated oil films. The effect of dispersant on hydroxyl radical concentrations was also studied. This research illustrates that the fate of oil and other dissolved species is impacted by photochemically produced reactive transients such as hydroxyl radical and singlet oxygen and that the presence of dispersant plays a role in controlling the transient behavior.

Photochemical Transformations of Petroleum on Seawater

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Crude oils from different geographic origins with varying chemical and physical properties were mixed with seawater and irradiated with simulated sunlight. The water-soluble organics (WSO) from irradiated water/crude oil samples were extracted and characterized by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), and compared to non-irradiated water/oil mixtures. Liquid-liquid extraction yielded two fractions from non-irradiated and irradiated water/oil mixtures: acidic WSOs (negative-ion electrospray, ESI), and base/neutral WSOs (positive-ion ESI). These fractions were analyzed by FT-ICR MS to catalogue molecular-level transformations that occurred to oil-derived WSOs after solar irradiation. In the WSO acid fraction, O2-O4 species predominated in the dark fraction whereas the irradiated fraction showed a distribution shift from O2-O10 centered around O4-O5. An increase in the overall abundance in the higher order oxygen classes in the irradiated samples of multiple oils indicates that photooxidized compounds become water soluble after irradiation. A wider range of oxygenated compounds were observed in the WSO acid fraction of more less viscous, heavy oils with higher API gravity.

Compositional Comparison of Weathering Trends for Four Different Spills Reveal the Unique Chemical Signature of Deepwater Horizon Oil Contamination

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Every oil spill is unique. More than four years after the explosion of the Deepwater Horizon oil rig, compositional changes that have occurred to the ~5 million barrels released have been catalogued, and a unique chemical fingerprint of oxygen-containing hydrocarbons has emerged. Biotic and abiotic modification to the parent Macondo well oil create ketone-containing oxygen compounds highly abundant in oil contamination collected from Gulf of Mexico beaches. Comparison of compositional changes that occur to parent and weathered oil derived from the Deepwater Horizon reveal a unique chemical signature determined by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry. Molecular-level characterization of compositional transformations that occur to oil derived from the M/V Cosco Busan spill (San Francisco Bay, 2007), the recent Kirby cargo spill (Galveston Bay, 2014), and other oil spills will be compared to Macondo-well derived oil contamination to catalogue the weathering trends for four different oil spills. Crude oil of different chemical and physical properties released in distinctly different geographic locations will be compared to chemical transformations of light, sweet Macondo well crude oil. Work supported by the National Science Foundation through DMR-1157490 and the BP/Gulf of Mexico research Initiative to the Deep-C Consortium.

Session 003
Microbial Ecosystem Trajectories in Gulf of Mexico Environments

Temporal and Spatial Patterns on The Northwest Florida Shelf: Implications for Microbial Response to Oil Spills

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Eighteen oceanographic research cruises were conducted along the Northwest Florida shelf between January 2011 and June 2014. Nine stations in each of three transects extending past the shelf break from Pensacola, Destin, and Panama City Beach were sampled. In addition to standard oceanographic parameters, bacterial biomass, bacterial production, phytoplankton production, chlorophyll a, and nutrients were measured. Microbial diversity from sequencing of PCR amplified rRNA genes was determined for bacteria, archaea, and ciliates. Distinct seasonal patterns were observed in summer stratification and winter water column mixing. Microbial biomass and production were observed to correlate and were related to nutrient availability. Microbial diversity also followed environmental parameters. For example, three main archaeal assemblages were observed: a seasonally independent near coastal assemblage, a seasonally dependent epipelagic assemblage, and a seasonally independent mesopelagic assemblage. The main environmental factors associated with archaeal community

structure were nutrients and salinity. In microcosm experiments bacterial response to oil, Corexit, and or solar radiation were found to be seasonally and location dependent. Oil and Corexit sensitive and resistant bacterial species were identified. These patterns were confounded by the presence of solar radiation. The results demonstrate that the Northwest Florida Shelf is a dynamic system and that the responses to environmental stressors are seasonally and location dependent making modeling and prediction of universal responses difficult.

Cable Bacteria: "Invisible" Sulfide Oxidizing Mats at Cold Seeps?

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Recently, a novel and remarkable sulphur oxidizing bacterial lifestyle was described in coastal marine sediments. Cable bacteria (family Desulfobulbaceae) grow as long filamentous chains encased in a continuous sheath and appear capable of conducting electrons across centimeter-scale distances from deep anoxic, reducing sediments to oxic surface sediments. By transporting electrons across steep redox gradients, these bacteria derive a high energy yield and can accumulate extensive amounts of biomass, with densities exceeding 2000 m of filament per cm2 of sediment. Unlike mats of other sulphur oxidizing bacteria, these potentially prolific bacteria are not visible from at the sediment surface. Cable bacteria have previously been found in coastal marine areas, especially in sulphide-rich sediments overlain by an oxygenated water column. Here, we provide evidence that cable bacteria exist at high densities near the sediment surface at an actively venting oil-rich marine seep in the Gulf of Mexico. We further show that by harvesting electrons from reducing sediment, cable bacteria cause extreme changes in porewater acidity, which could have critical consequences for both microbial community associations, material fluxes of redox active compounds at seepage areas, and carbonate preservation. The role of cable bacteria in structuring microbial associations and affecting sediment geochemistry in surficial sediments at oily seeps has been overlooked to date, but they may impart a broad and significant signature at the seafloor of these environments.

The Deep-Sea Water-Sediment Interface: Eukaryotic Microbial Communities from the NE Gulf of Mexico

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Studies of eukaryotic marine microbes have mostly targeted either water column or sediment samples. Fine grained silt and clay material, common to deeper sea sediments, limits pore space for interstitial organisms thereby supporting an assumption that interstitial microfauna such as larger ciliate protists, common to marine sands, are not important to the deep-sea benthos. Consequently, we have targeted the water over cores (WOC), collected by a multicorer in the NE Gulf of Mexico (GOM), to obtain material representing the nephaloid layer of the sediment surface as a potentially important interface for microbial activity. DNA was extracted from 0.2 µm filtered WOC samples. Sequences obtained for ciliate protists indicate a majority (~75%) of the cloned sequences corresponded to existing, yet unclassified, sequences in databases. The data also defines the presence of organisms unique to WOC samples and not found in filtered deep water column samples, taken by niskin bottles, at the same stations. From cloned sequences named in the database (~25%), there is a mix of known planktonic ciliates and many known interstitial benthic ciliates including Hypotrichs and Stichotrichs, and

Litostomes. These organisms document an active benthic ciliate community that is typically excluded from the pore space of the fine grained muds but here recovered from the nephaloid sediment-water interface. In WOC samples collected 3 years after the spill, species richness of the ciliates increased with the increasing concentration of PAHs in the upper 2 mm of the sediments, suggesting that these communities may be indicative of microbial degradative response to the elevated petroleum hydrocarbon inputs and associated organics from the BP well failure.

Short-chain Alkane Production in Gulf of Mexico Cold Seep Sediments

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The organic-rich cold seep sediments in the deep Gulf of Mexico commonly contain mixtures of light hydrocarbon gases either dissolved in pore fluids, adsorbed to sediment particles, trapped in methane ice, or as free gas. The dominant component in these natural gas mixtures is typically methane (C1), but ethane (C2) and propane (C3) are nearly always present in trace or major amounts. The ratio of C1:C2:C3 varies but C2 and C3 are typically present at single digit percent levels, whereas methane usually dominates at >80%. Production of ethane and propane in deep-sea sediments has been historically attributed only to thermocatalytic processes, but carbon isotopic ratios of ethane and propane from deep cores from the Gulf of Mexico suggest alkanogenesis at depth in the sediment column and alkane oxidation in uppermost oxidant-rich sediments. Limited experimental work suggests production of C2/C3 compounds through the activity of archaea, though such studies of microbial- driven dynamics of C2/C3 gases (i.e. 'alkanogenesis') in cold seep sediments are rare. Furthermore, the identities of potential substrates are poorly constrained and no attempt has been made to quantify production rates of C2/C3 gases. Here, we present the results of a series of incubation experiments using sediment slurries culled from GC600, one of the most prolific natural oil and gas seeps in the Gulf of Mexico. Rates of both alkane production and oxidation were measured under a variety of conditions to assess the net rates of alkane production and elucidate the driving microbiological mechanisms and controls on the central processes of >C1 alkane cycling in cold seep sediments.

Microbial Enzymatic Activity and Secondary Production in Sediments Affected by the Sedimentation Pulse following the Deepwater Horizon Oil Spill

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We measured heterotrophic microbial metabolic rates as well as porewater and sedimentary geochemical parameters at sites proximate to and distant from the wellhead to investigate benthic microbial responses to the "Dirty Blizzard" in Nov/Dec 2010. Lipase activity and rates of bacterial protein production were highest and leucine-aminopeptidase activity was lowest in 0-2 cm sediment layers at the sites proximate to the wellhead. These results suggest that the presence of the oil snow stimulated benthic microbial enzymatic hydrolysis of oil-derived organic matter that was depleted in peptide substrates at the time of our sampling. The strong gradients in porewater DOC, NH4+, and HPO43- concentrations in the upper 6 cm of the sediments near the wellhead likewise indicate elevated heterotrophic responses to recently-sedimented organic matter. In addition to enhanced microbial activities in the 0-2 cm sediment layers, we found peaks of total organic carbon and elevated microbial metabolic rates down to 10 cm at the sites closest to the wellhead. Our results indicate distinct benthic

metabolic responses of heterotrophic microbial communities, even three months after the ending of the 'Dirty Blizzard'. Compared to other deep-sea environments, however, metabolic rates associated with the recently deposited particulate matter around the wellhead were only moderately enhanced. Oil contaminants at the seafloor may therefore have prolonged residence times, enhancing the potential for longer-term ecological consequences in deep-sea environments.

Biogeography of Phytoplankton Community Structure in the Northern Gulf of Mexico

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The northern Gulf of Mexico is a dynamic and diverse ecosystem that is driven by a complex circulation pattern. The Mississippi River plume is rich in nutrients and delivers 90% of total nitrogen load and 87% of total Phosphorus load to the basin. The plume flows mostly close to the coast over the continental shelf although during years of high discharge, it has been observed flowing south past the Florida Keys and even as far as off the coast of Georgia. The loop current on the other hand is depauperate in nutrients and can shed large mesoscale eddies with attendant smaller scale features. In addition, we have also shown that natural oil seeps in this region can enhance phytoplankton abundance. These large and small scale forcings result in high spatial and temporal variability in the phytoplankton community structure. We used an Advanced Laser Fluorometer to measure highly resolved phytoplankton pigment composition and fluorescence due to Colored Dissolved Organic Matter (CDOM) in the northern Gulf of Mexico over five cruises between 2010 and 2013. We will present the results of this study and discuss the biogeography of phytoplankton in the northern Gulf of Mexico.

Elucidating the Diversity of Benthic Microbial Communities and Foraminifera at the Seafloor in the Northern Gulf of Mexico

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A substantial, but still uncertain, fraction of oil from the Deepwater Horizon (DWH) disaster was transported to the seafloor, possibly resulting in chronic impacts to these sensitive benthic ecosystems. Assessing such impacts is challenging since deep sea sedimentary ecosystems are vastly understudied in comparison to their planktonic counterparts. Through a strong cross-consortium effort, a time series of data that included microbial and benthic foraminiferal community characterization along with sedimentary redox conditions for deep ocean sediments across the northern Gulf of Mexico was interrogated following the DWH oil spill. Microbial community structure was determined through the generation of 80 million Illumina amplicon sequences from over 700 samples representing 23 sites across a 3 year time period. From a subset of these sites, benthic foraminiferal assemblage dynamics were investigated through high-resolution sediment sampling spanning a longer time scale. Preliminary results reveal that benthic communities are similarly structured along gradients in oxygen availability and redox chemistry, which are likely controlled by carbon delivery and sediment grain size. This study contributes to our fundamental understanding of the natural variation in benthic ecosystems, which is

necessary for predicting the long term impacts of oil deposition from accidental discharges. Continued monitoring of key sites will be critical to assess the recovery of these systems.

Geographical and Geological Distribution of Benthic Bacterial Communities in the Gulf of Mexico after 2010 Deepwater Horizon Oil Spill

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Benthic bacterial communities play a crucial role in nutritional recycling in oceanic environments. Organic matter is decomposed by the benthic bacteria, which then serves as a source of nutrients for other micro- and macroorganisms. The benthic bacterial community is generally stable as long as they are not influenced by anthropogenic disturbances. It is believed that the Deepwater Horizon (DH) oil spill greatly influenced the benthic bacterial community, while it is not clear what changes have been made in the benthic bacterial community years after the spill. This research is conducted to address this question by monitoring bacterial communities in benthic sediments collected along the continental shelf of the northern Gulf of Mexico. Sediment for this study was collected on the NOAA ship Pisces in Oct/Nov 2013 using a multicorer. Total DNA extracted from benthic sediments samples were analyzed by denaturing gradient gel electrophoresis (DGGE) of bacterial 16S rRNA gene amplicons. The resulting images were further analyzed by the software PyElph version 1.4 (http://pyelph.sourceforge.net/) with UPGMA (unweighted pair-group method using arithmetic averages) clustering algorithms. Our data demonstrated that the bacterial communities in benthic sediments collected near and along the current flow from the mouth of Mississippi River show distinct community structures, compared with those of benthic sediments on the shelf of the Florida panhandle. This study suggests the benthic bacterial community is significantly influenced by the influx of the Mississippi River three years after the DH oil spill. This research was made possible by a grant from BP/The Gulf of Mexico Research Initiative.

Response of Deep-sea Sediment Bacterial Communities in the Gulf of Mexico to Light Louisiana Sweet Crude Oil

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It is known that oil-degrading bacteria can quickly develop in the deep seawater of the northern Gulf of Mexico for the intrinsic bioremediation of the crude oil released by the Deepwater Horizon (DWH) oil spill. However, the response of bacterial communities in the deep-sea sediments, where a significant portion of oil was deposited, has received limited attention. To determine the bacterial community dynamics and degradation rate of non-dispersed (200 ppm) and dispersed (200 ppm, Corexit dispersant oil ratio of 1:20) Light Louisiana Sweet crude oil, we incubated surface deep-sea sediments (~2 cm) collected near the Macondo wellhead in the laboratory at 4℃ for 6 months. Total DNA and petroleum hydrocarbons were extracted from the sediment after 0.5, 1, 2, 4, and 6 months, and analyzed by high-throughput tag sequencing. Our results show that the oil-amended sediments had higher abundances of Gammaproteobacteria and Alphaproteobacteria. Among the Grammaproteobacteria, members of Alteromonadales, Oceanospirillales and Methylococcales showed the largest increase in relative abundance, while Alphaproteobacteria was represented by an increase of Rhodobacterales. The addition of dispersant Corexit did not cause an apparent shift in microbial community structure. Our findings suggest that potential oil degraders in the surface deep-sea sediments closely resemble that of

the plume. These insights help further our understanding of the key microbial players in the sediment over the course of the DWH spill. GC/MS data on residual alkanes and polycyclic aromatic hydrocarbons (PAHs) will also be presented.

Deep Sea Coral-Associated Bacterial Community Composition Analysis Using 16S rDNA

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There is a growing recognition that deep-sea corals are much more than simply animal tissue and that their physiology can be modified and enhanced by their symbionts. In shallow water corals, both dinoflagellate and bacterial symbionts are fairly well characterized. However, in deep water corals, which lack Symbiodinium dinoflagellates, the importance of bacteria is still largely unknown. With that in mind, the goal of this work was first to characterize the microbial communities associated with the deep-water black coral Leiopathes glaberrima, testing for a consistent group of bacteria associated with the species, and second to test for the effects of oil and dispersant exposure on bacterial diversity. 24 16S amplicon libraries were analyzed via the Illumina MySeq platform, consisting of 16 samples from an oil and dispersant exposure experiment and 8 untreated samples from two different sites. Full results from this data will be presented, with preliminary results indicating that bacterial species are mostly uncultured, but commonly align with Endozoicomonas and other gamma-proteobacteria. The next step in this research will be to analyze a variety of coral species from our collections to determine the consistency of the community composition across both geographic and phylogenetic distance, as well as examining the link between natural seeps and coral-associated bacterial diversity.

Temporal Changes of Oil-degrading Bacteria in Louisiana Salt Marsh Sediments after the Deepwater Horizon Oil Spill

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The Deepwater Horizon (DWH) event oiled more than 650 miles of Gulf coastal habitats, with Louisiana salt marsh being most severely contaminated. This study was to determine the changes of oil-degrading bacterial populations in the slightly and heavily oiled Louisiana marsh sediments over a course of 30 months following the DWH spill. Quantitative real-time PCR (qPCR) analysis revealed that the relative abundance of the n-alkane degrading bacteria generally decreased over time, while that of the polycyclic aromatic hydrocarbon (PAH) degrading bacteria increased. The oil-degrading communities were increasingly dominated by gram-positive (GP) PAH-degrading bacteria over time and 29 months after the spill, more than 99% of the oil degrading genes detected (i.e., alkB, GN PAH-RHDα, and GP PAH-RHDα) were from GP PAH-degraders. The 16S rRNA sequencing of oil-degrading bacterial strains isolated from samples taken 30 months after the spill identified that 66% of the isolates were GP, with nearly half belonging to Firmicutes. The observed shift in microbial populations over time and the dominance of gram-positive PAH-degraders is indicative of a later stage of the biologically driven attenuation of hydrocarbon-contaminated soils. The present study implies that two and one-half years after the DWH oil spill the oiled Louisiana salt marsh sediment has come into its latter stage of naturally microbial attenuation.

Session 004
Applications of Research in Oil Spill Fate and Transport Modeling for Decision Support

Lagrangian Trajectories Computed using the ROMS Model in GoM during the BP Oil Spill: Verification and Sensitivity Quantification using the Bred Vector Technique

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The ROMS model with floats is used to simulate the particle trajectories during the BP Deepwater Horizon oil spill in the Gulf of Mexico. HYCOM analysis is used as the initial and boundary conditions. The Bred Vector Technique is used to generate an ensemble of initial conditions valid on 20 April 2010. A control forecast with a lead time of three months is launched from 20 April in which floats placed at every 9 km at the surface of GoM are advected. The ensemble of initial conditions is used to generate 20 different trajectories for each float over the same lead time. The sensitivity quantified by the spread in ensemble trajectories ranges from about 20 to 200 km with the highest spread in the loop current region. The control forecast and ensemble mean forecast are verified against a trajectory generated with an offline algorithm using the HYCOM analysis currents. The ensemble mean improves over the control forecast by about 10 km to 50 km in the RMSE. In another experiment floats are released at the spill location every hour for two weeks and the location of these floats after three weeks is used to quantify the spread of oil. The ensemble runs are used to attach probabilities to the amount of oil at different locations. It is seen that the probability of the oil escaping the GoM via the Gulf stream is very low. The results demonstrate that operationalizing such a probabilistic forecasting system would benefit relief operations in the event of a spill in the future.

Deepwater Blowout and Response Modeling in Support of Strategic Spill Response Planning and Execution

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Injection of subsurface dispersants during well blowout event is now supported by models of the change in droplet size distribution, and, thus, the change in the oil mass balance between the surface and subsurface ocean. Improvement in Human Health and Safety (HSE) is a significant bonus of this response method. This is now an accepted tool within the framework of response options. Subsurface dispersant injection has been added the suite of response modeling in the SINTEF Oil Spill Response And Contingency (OSCAR) model. Decision-making in both planning and execution of oil spill response actions will benefit from improved estimates of the effectiveness of each response strategy, and thus models of individual response options can be combined and applied to an event. For mechanical recovery, surface dispersant application (vessels and/or aircraft), and in situ burning, such measures are intended to change the distribution and thickness of oil slicks on the sea surface. For dispersant injection at the source, the additional changes to the resultant distribution of hydrocarbon concentrations in the water column and any reduction in air hazard to response personnel are significant factors to consider. This paper will use the SINTEF OSCAR model, with the integrated underwater blowout module, to

demonstrate the potential such response tools have for providing useful input to oil spill contingency planning and response.

Near Field LES Simulation of Bubble Plumes in Oil Blow-outs: Statistical Analysis and Cross Flow Influence

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Oil blow-outs at large depths involve many complex physical phenomena such as multiphase flow dynamics, intrusion into stratified layers of fluid, jets in cross flow and gas-liquid interaction. Regarding the latter, a significant portion of the oil-well is filled with gas and, when broken, the resultant bubble plume has an important effect on oil dispersion and mixing with the ambient fluid. In this study a Large Eddy Simulation in-house code is used for the simulation of bubble plumes. The code has undergone several refinements with the purpose of obtaining a highly accurate and reliable CFD tool and yet very optimized in terms of time and computational resources so that it can be applied to practical engineering cases. These developments are, a strongly-coupled Lagrangian Particle Tracking (LPT) algorithm operating in an Eulerian flow field and a hybrid MPI-OpenMP parallelization strategy that alleviates the enormous computational overhead of the LPT routines. The code is applied to bubble plume simulations in both stagnant fluid and a cross flow. The code is initially validated with experimental data from collaborative work undertaken at Texas A&M. The simulation results show a very good agreement with the experimental data in terms of plume size, flow patterns and first- and second-order statistics. The simulations are then extended to study the effects of the cross-flow on the bubble plume dynamics. Special interest was made on the influence of the cross flow velocity on the channel's secondary flow and the plume's shape and inclination.

A New Approach for Studying Oil Dispersion over Large Domain Sizes using Large-eddy Simulation

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Large-Eddy Simulation (LES) has proven to be a valuable tool in producing high-fidelity simulations of important processes in the ocean mixed layer (OML), such as Langmuir turbulence, because LES can explicitly resolve most turbulence on the computational grid representing detailed physics accurately. LES horizontal domain sizes are typically restricted to a few kilometers due to the high computational cost. This limitation is not a major issue for the prediction of the velocity field, because the small depth of the OML (smaller 100 m) limits the size of flow. However, the complex interaction among Langmuir cells, turbulence, and Ekman transport gives rise to oil plumes displaying features on scales larger than a few kilometers. A new approach is proposed to tackle this problem with currently available computing power. The approach consists of: i) using LES with periodic boundary condition in horizontal directions to simulate the ocean flow in a domain of a few km in each direction; ii) using the periodicity of the velocity field to extend the domain size in both horizontal directions; iii) using the extended domain to simulate the plume dispersion. This approach can be implemented in a computationally efficient algorithm by defining several oil concentration fields that interact via boundary conditions. Results using this new approach will be presented and compared to simulations using the traditional approach. This study is supported by a GoMRI RFP-II grant.

Development of a New Oil Droplet Biodegradation Algorithm for NOAA's Oil Spill Modeling Suite (GNOME/ADIOS)

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In recent years, it has become apparent that the rate of biodegradation of oil in the environment is of great concern to oil spill responders and the community. While it has been accepted that the long term fate of most oil in the water column is dominated by biodegradation, the rates of degradation have been poorly understood, and the tools to model the process have been limited. Many environmental factors have been shown to have an effect on biodegradation rates, including temperature, nutrient load, composition of the microbial community, oil composition, and overall surface area of the oil-water interface. However, the interplay between these effects remains unclear. As part of the process to upgrade the weathering algorithms in NOAA's oil spill modeling suite, we have developed a new rate law to model the biodegradation of oil droplets based on Monod kinetics. Surface area of the droplet is explicitly included as a parameter that changes over the course of a modeling run, while oil composition is accounted for by using pseudocomponents with distinct mass fractions and biodegradation rate constants. All other environmental factors that affect biodegradation are incorporated into the rate constants for each component. The values for these rate constants are derived from published experimental studies. More systematic studies are needed in order to determine the exact nature of these effects on biodegradation rates of oil.

Uncertainty Propagation in an Oil Plume Model

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Predicting oil spill fate and transport with uncertainties is important for decision support. This work applies the methods of Polynomial Chaos Expansion (PCE), Gaussian Process Regression (GPR) and Monte-Carlo (MC) sampling to quantify the forecast uncertainties in an integral oil plume model simulating the Deepwater Horizon oil-gas blowout. Our main goal is to propagate the input and model parametrization uncertainties and access the detailed statistical characteristics of the model outputs efficiently. PCE and GPR methods only need around 500 simulations instead of 50,000 simulations using MC method and the result agrees very well. The experiments focus on five uncertain input parameters and several model output uncertainties: the oil/gas plume trap height, peel height and the gas distribution at the trap height. The probability density functions of these outputs and their sensitivity indices are estimated. Sensitivity analysis shows the crucial parameters affecting the oil/gas behaviors are the entrainment parameters. Better agreement with fluorescence measurements is seen in the experiment with a smaller range of 95th percentile oil droplet/gas bubble sizes that simulates the effect of chemical dispersant.

Quantifying Uncertainty in the Deep-C Oil-Fate Model Using Polynomial Chaos

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An ensemble-based polynomial chaos (PC) method is used to propagate the input uncertainty of the Deep-C Lagrangian oil-fate model, and to estimate its output uncertainties. The PC approach constructs a series-based surrogate for the model, which is then used to estimate the model statistics. Two sources of uncertainty were considered in a deep-water blowout simulation. One is the oil droplet size distribution controlling the droplets rise velocity, and where the uncertainties are the spread and 95 percentile parameters of a Rosin-Rammler distribution. The other sources of uncertainties considered were the advecting ocean currents, which were given by the outputs of a 1/25 General Ocean Circulation Model. The ocean currents were perturbed through their two dominant Empirical Orthogonal Functions. Sensitivity analysis shows that ocean currents dominate the uncertainty in the predicted oil concentration at the surface, but the oil droplet size distribution controls the oil concentration at depth. The surrogate was used to produce probability maps of the oil concentration considering the input parameters, which is important to establish confidence levels on the predictions.

Predicting Oil Transport Clustering, the Evolution of Surface Material Density

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Ocean-driven oil transport leads to clustering, which is the process of increasing material density due to convergence at the surface. Clustering presents an opportunity to collect material more efficiently. We present new work providing insight into the ocean processes contributing to clustering, evolution of clustering over time, the material structures that form on the ocean surface, and the ability to predict clustering. To understand clustering across scales, we implement a telescoping series of nested ocean models at resolutions of 3 km to 50 m providing features from 500 km to 500 m in conjunction with the GLAD and SCOPE drifter experiments of the CARTHE consortium. Clustering is illuminated through advection of inert particles at the ocean surface. The ability to predict clustering depends on the ocean process and the observations available to constrain a numerical model forecast. Satellite remote sensing constrains transport by eddies to a degree, and drifter observations serve as a strong in situ constraint. The processes along ocean eddy fronts drive clustering, and these are deterministically driven by the eddy field. The shelf break front exhibits high nondeterministic variability that is very difficult to predict. Topographic interactions control clustering on the shelf, and thus is predictable give the bathymetry and forecast currents. With an understanding of clustering, we can envision optimizing strategies for collecting or dispersing surface material by taking into account the prediction of dominant ocean processes at a particular place and time.

Uncertainty Modeling and Reliability Assessment for Operational Oil Spill Forecast

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Oil spill accidents are man-made disasters which lead to severe environmental damage and significant financial losses. To minimize the consequences, rapid response plays a critical role, whereas herein the operational oil spill forecast is the core process. The state of the art 3D hydrodynamic models along with oil spill transport models have escalated the efficiency of rapid response into an information and numerical age. However, challenges in the blithe application of such numerical oil spill forecast modeling can be met due to uncertainties from various sources. These uncertainties may include: 1) geometrical uncertainty (Does the model grid well represent the real physics?), 2) initial and boundary forecast data uncertainty (Are forecast data close to the observations?), 3) structural uncertainty (Do the PDEs precisely model the physics?), 4) parameter uncertainty (How accurate are model parameters?). Understanding uncertainty representation, propagation, and the reliability of a numerical forecast becomes crucial for better oil spill contingency planning. We implement a comprehensive sensitivity with different model set up and input forecasts for uncertainty identification. Some new terms are proposed to quantify the forecast uncertainty based on the Monte Carlo simulation. A statistic model is created to assess the reliability of a simulation given the forecast period.

A Vision of Science for Next Generation Response

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Science for Decision Support is directed toward illuminating the situation space in order to more clearly define environmental indicators and predictions for use in selecting among options, including no response. The modelers and analysts must also provide the information to advise the decision makers on possible consequences between "no" and "no go" options. Tradeoffs frequently exist in selecting among response options. Examples are:

•"How clean is clean?" to determine the end point for beach cleanup in order to balance oil removal with biological harm.

•Application of chemical dispersants to control the distribution of oil mass between the surface and subsurface. The presence of any sensitive surface marine resources, e.g. birds and wildlife, must be balanced with the presence of sensitive aquatic species, such as corals or larval fish. These are similar whether the dispersant is applied at the surface or subsurface.

Decision makers must select among available options to balance maximizing environmental benefit vs. causing harm.

Next generation response includes advancement on five fronts, with examples included

• Updated environmental/situational information: social media, real-time data;

• Predictive Tools: droplet size distribution, dynamical systems theory, ice transport modeling, real-time modeling;

• Response Options: manipulation of droplet size distribution through use of surface and/or subsea chemical dispersants;

• Consequence analysis (Effects, trade-offs): biodegradation, larval fish modeling, economic impacts;
• Communication: Visualization, Data Integration, Common Operational Picture (COP).

Session 005
Gaps to Gains: Transdisciplinary Approaches in Examining Environmental, Health, and Ecosystem Services Risk and Resilience in Gulf Coast Communities

Responses to the Gulf Oil Spill: Health Research, Community-Academic Partnerships, Lessons Learned, and Preparedness for Future Disasters

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Historically, studies of major oil spills have no measures of exposure and only track health impacts among workers. Typically, this is true of most disasters. NIH and NIEHS intramural and extramural funded investigators, in partnership with community groups, have engaged in research efforts to better understand the health impacts of the Gulf Oil Spill including epidemiologic investigations of over 32,000 clean-up workers (GuLF Study) and other at-risk community populations, large-scale exposure reconstructions, research into seafood contamination and polycyclic aromatic compounds, and development of education and training efforts. Early findings underscore the need for further investigation to understand the long-term effects on established cohorts, risk factors, and biomarkers that contribute to community and individual resiliency or vulnerability. The evolution from design to implementation, in combination with innovative community-academic partnerships, affords an opportunity to share key findings and chart new strategies to unravel the complex interplay between human health and the environment. Additionally, using these new platforms and “lessons learned” we can begin to translate “research to practice” to help promote environmental health literacy, improve environmental and human health baselines, and further our understanding of the physical and psychosocial effects. Lastly, development of ongoing multidisciplinary research and collaborations will help to improve the health and wellbeing of Gulf Coast communities and better prepare us to address the challenges of acquiring timely health data to improve our preparedness and response during future disasters.

Experience of the Deepwater Horizon Oil Spill and Mental Health in Pregnant and Reproductive-aged Women

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Experiencing technological disasters can be associated with worse mental health. 889 pregnant and reproductive-aged women were recruited from southern Louisiana areas affected by the Deepwater Horizon oil spill. Women were interviewed about their exposure to oil and personal effects of the oil spill, and completed the Edinburgh Depression Scale and the Post-traumatic Stress Checklist. Factor analysis was used to group questions about oil spill experiences. Log-linear and logistic models were used to assess the relative risk of worse mental health associated with oil spill experiences, adjusted for

age, income, race, gravidity, and proximity to the coast. 15.4% met the criteria for likely depression, and 7.4% for likely PTSD. Most strongly associated with depression were direct contact with oil (adjusted relative risk [aRR], 1.74, 95% confidence interval [CI] 1.25-2.43); financial loss (aRR for reporting all 4 indicators, 2.56, 95% CI 1.49-4.39); and the combination of property damage and knowing someone who was injured/killed (aRR 4.77, 95% CI 2.58-8.83). Most strongly associated with PTSD the combination of property damage and knowing someone who was injured/killed (aRR 2.19, 95% CI 1.27-3.79); direct contact with oil (aRR 1.88, 95% CI, 1.14-3.09); and any financial loss due to the spill (aRR 1.80, 95% CI 1.10-2.97). There was a suggestion that more involvement in litigation was associated with depression (aOR 1.57, 95% CI 1.00-2.45) but not PTSD (aOR 1.12, 95% CI 0.60-2.12). Future directions include identifying protective factors that improve outcomes among those who are highly exposed.

Quality of Life as a Measure of Resilience in First-time Gulf Coast Pregnant Women

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BACKGROUND: The Transdisciplinary Research Consortium for Gulf Resilience on Women's Health at Tulane University implemented a community-based participatory research project to assess the impact of the Deepwater Horizon oil spill on reproductive health in disaster-prone and low-income Gulf communities. OBJECTIVE Determine the effect of pregnancy on physical and mental health in WIC-eligible, first-time mothers in Southeast Louisiana. METHODS: The longitudinal intervention equipped Community Health Workers (CHWs) with mobile technology to facilitate data collection, health education and resource distribution. Underserved pregnant women (N=96) completed self-administered SF36 Quality of Life Assessment during each trimester. RESULTS: The cohort was predominately <29 years old (88%), African-American (63%), urban (77%), single (61%), high school educated (57%), and enrolled in Medicaid (63%). With exception of physical functioning, SF-36 subscales varied significantly by trimesters: role physical ($p<.0001$), bodily pain ($p<0.0001$), general health ($p=0.04$), vitality ($p<0.0009$), social functioning ($p=0.03$), role emotional ($p=0.01$), and mental health ($p=0.03$). Compared to the general US female population ages 18-34, participants had higher vitality and mental health across all trimesters ($p<0.05$). DISCUSSION: Our findings suggest quality of life varies across trimesters. Additionally, pregnant women supported by technology-enabled CHWs showed increased resiliency as measured by vitality and mental health components of the SF-36.

An Analysis of the Impacts of the Deepwater Horizon on the Seafood Industry

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This research was carried out for the Bureau of Ocean and Energy Management to assist them in understanding the economic impacts the Deepwater Horizon Oil spill had on the Gulf of Mexico seafood industry. In addition to an extensive research effort compiling all research pertinent to the Gulf seafood industry structure from vessel to market we have reviewed and compiled available economic impact publications pertinent to the commercial fishing industry. In context to this information and various other economic data and model sources we have developed an input/output impact model that calculates these impacts as they occur down the seafood supply chain. Impacts have been broken down by each Gulf State and key species category, with estimates of direct, induced and indirect impacts on

Sales, Value Added, Employment and Income. The primary contribution of this research was laying out the supply chain relationships and market structure to allow for a better understanding how economic impacts occurred during the post spill period.

Respiratory Symptoms in Oil Spill Clean-up Workers Participating in the GuLF STUDY

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BACKGROUND: Oil spill clean-up workers may be exposed to respiratory toxicants. We studied respiratory symptoms in the GuLF STUDY, a cohort of 32,736 adults who worked or sought work in oil spill clean-up after the Deepwater Horizon disaster. METHODS: Demographic, exposure, and health information was collected in telephone interviews 1-3 years after the disaster. Participants were asked how often they had specific symptoms in the 30 days before the interview. We calculated adjusted prevalence ratios (PR) and 95% confidence intervals (CI) for associations between frequent symptoms ("most" or "all of the time") and qualitative levels of oil exposure using log-binomial regression. Covariates included demographic and socioeconomic factors, smoking, prior lung disease, and residential proximity to the oil spill. Results: Symptom prevalence was chest tightness 6%, shortness of breath 9%, wheeze 10%, and cough 16%. The prevalence of symptoms was increased for those who did any clean-up work compared to those who did not. For wheeze, PR were 0.91 (0.80, 1.04), 1.24 (1.11, 1.39), and 1.66 (1.53, 1.81) for workers reporting low, medium and high exposure jobs compared to nonworkers after taking into account covariates noted above. Trends were similar for other respiratory outcomes. CONCLUSIONS: Oil spill clean-up workers reported increased prevalence of respiratory symptoms compared to nonworkers. Ongoing efforts to better characterize spill-related exposures and longer follow-up will further clarify observed associations.

Communicating Current Biomonitoring Results to Gulf Coast Residents

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There have been ongoing concerns among Gulf Coast residents about potentially higher levels of exposure to oil-spill related chemicals. An important byproduct of the NIEHS GuLF STUDY was the opportunity to collect information about environmental exposures through biological samples and exposure monitoring. To address community concerns and characterize contemporaneous environmental exposures, we measured blood levels of metals and volatile organic compounds in 1,077 GuLF STUDY participants who resided in Alabama, Florida, Louisiana, or Mississippi. We identified potential determinants of exposure levels, and designed a strategy for communicating biomonitoring results that included disseminating a personalized report to each participant. The aim of the current study was to contextualize how biomonitoring results and knowledge about current chemical exposures were communicated to, and understood, by Gulf Coast residents. To evaluate the effectiveness of the report-back process in communicating results and exposure reduction strategies, a subset of study participants were sampled for a semi-structured follow-up interview. The interview guide included

questions that addressed individual biomonitoring results and perceptions about current Gulf Coast exposures. Using qualitative methods, we identified key areas to consider when disseminating biomonitoring study results. This presentation will highlight effective strategies for communicating biomonitoring results and exposure reduction strategies to residents of communities affected by oil spills.

Lung Function in Oil Spill Clean-up Workers and Non-Workers in the GuLF STUDY Cohort

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BACKGROUND: Oil spill clean-up workers may have exposures leading to decreased lung function. Objective: Evaluate the association between oil spill clean-up work and lung function following the 2010 Gulf Oil Spill. METHODS: Data were obtained from the Gulf Long-Term Follow-Up Study (GuLF STUDY), a prospective cohort study of workers who worked at least one day on oil spill clean-up and non-workers. Participants residing in the Gulf region who completed an acceptable pulmonary function test were included in the study (N=5,711). Three pulmonary function measures were analyzed: forced vital capacity (FVC), forced expiratory volume in 1 sec (FEV1), and the FEV1/FVC ratio. Multivariable linear regression was used to estimate the association between exposure and lung function. Models adjusted for age, age squared, height, height squared, race/ethnicity, education, employment, income, and previous clean-up work. RESULTS: Among women, no significant differences in lung function were found. Among men, those exposed had a higher FEV1/FVC ratio compared to unexposed (β: 0.007, p= 0.017). CONCLUSION: Results may reflect a “healthy worker” effect; further research is needed to characterize the relationship between levels of exposure to oil-related compounds and lung function among those who worked. Job/task-specific exposure estimates are currently being developed using ambient measurements collected at the time of the spill. Analysis of lung function in workers in relation to these estimates is ongoing.

Chemical and Non-chemical Stressors Linked with the Gulf of Mexico Oil Spill and the Impact on Telomere Length, a Biological Marker of Stress and Health, in Infants and Young Children

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Using Secondary Data to Quantify the Health Impacts of Disasters in the Gulf

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INTRODUCTION: Quantifying the health impacts of disasters can be difficult without expensive and time consuming primary data collection. However, available secondary data can be utilized to estimate the impacts of disasters on health and health systems and to examine trends related to health status and

health system utilization over time. METHODS: The Centers for Medicare and Medicaid Services (CMS) Geographic Variation Public Use File (GVPUF) contains 100 percent of Medicare claims aggregated to the county level for calendar years 2008-2012. GVPUF contains demographic variables, data on the prevalence of 19 chronic conditions, as well as spending and utilization data. To determine the association between hazard exposure and health system utilization and control for time-invariant confounders we used a fixed effects regression model to conduct within county comparisons in 2010 and 2011 in five Gulf States (Texas, Louisiana, Mississippi, Alabama, and Florida) affected by Deep Water Horizon (DWH). RESULTS: Overall, health system utilization (e.g., inpatient, rehabilitation, home health) by Medicare beneficiaries age 65 or older in the five Gulf States was inversely associated with disaster exposure. However, health system utilization increased in subsequent years. Several health outcomes were also significantly associated with hazard exposure, including depression. DISCUSSION: Health system utilization by Medicare beneficiaries was reduced in the time following the Deepwater Horizon disaster. This may be related to limitations in access. Further research is needed to fully understand the implications of these findings.

Community-Based Participatory Research in Southeast Louisiana: Challenges in Determining Air and Food-Borne Exposures in Low-Income Participants

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To better inform individuals as to what chemicals are in their indoor and outdoor air, we have been conducting home assessments involving participants in risk analyses. We have also been analyzing seafood or fish samples of most interest to participants for the presence and levels of polycyclic aromatic hydrocarbons (PAHs) including many that are specific to crude oil. Preliminary results indicate that levels of the selected volatile organic compounds are generally higher in indoor air samples when compared to paired-outdoor air samples. Seafood and fish analyses do not support the presence of PAHs at any levels that would represent a consumption health risk. We will discuss the implications of our findings to date and how involving individuals in the risk analysis/assessment process may aid informed decision-making. We will also focus our discussion on the challenges that have been encountered in engaging participants in southeast Louisiana in community-based research as well as challenges involved in maintaining participation once enrolled.

A Targeted Risk Assessment following the Deepwater Horizon Oil Spill: Polycyclic Aromatic Hydrocarbon Exposure in Vietnamese- American Shrimp Consumers

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BACKGROUND: The Deepwater Horizon oil spill of 2010, prompted concern about health risks among seafood consumers exposed to polycyclic aromatic hydrocarbons (PAHs) via consumption of contaminated seafood. OBJECTIVE: To conduct population-specific probabilistic health risk assessments based on consumption of locally harvested white shrimp (*Litopenaeus setiferus*) among Vietnamese-Americans in Southeast Louisiana. METHODS: We conducted a survey of Vietnamese-Americans in Southeast Louisiana, to measure shrimp consumption, preparation methods, and bodyweight among

shrimp consumers in the disaster-impacted region. We also collected and chemically analyzed locally harvested white shrimp for 81 individual PAHs. We combined the PAH levels (with accepted reference doses) found in the shrimp with the survey data to conduct Monte Carlo simulations for probabilistic non-cancer health risk assessments. We also conducted probabilistic cancer risk assessments using relative potency factors (RPFs) to estimate cancer risks from the intake of PAHs from white shrimp. RESULTS: Monte Carlo simulations were used to generate hazard quotient distributions for non-cancer health risks, reported as mean +/- standard deviation, for naphthalene (1.8 x 10-4 +/- 3.3 x 10-4), fluorene (2.4 x 10-5 +/- 3.3 x 10-5), anthracene (3.9 x 10-6 +/- 5.4 x 10-6), pyrene (3.2 x 10-5 +/- 4.3 x 10-5), and fluoranthene (1.8 x 10-4 +/- 3.3 x 10-4). A cancer risk distribution, based on RPF-adjusted PAH intake, was also generated (2.4 x 10-7 +/- 3.9 x 10-7). CONCLUSIONS: The risk assessment results show no acute health risks or excess cancer risk associated with consumption of shrimp containing levels of PAHs detected in our study, even among frequent shrimp consumers.

Maintaining Natural Habitats and Biodiversity Could Increase Resilience of Gulf of Mexico Coastal Communities and Support Human Health and Well-Being

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Human health and well-being is the ultimate/cumulative ecosystem service. Incidents such as the Deepwater Horizon oil spill remind us that in ecosystems such as the Gulf of Mexico, where strong multiple stressors reduce the quantity, quality, and stability of ecosystem services and increase variability in their delivery, we can expect increased negative effects on the resiliency and health of individuals and communities. These can include significant impacts to natural resources and biodiversity which lead to declines in jobs, recreational opportunities, food security, coastal protection, and other effects which in turn cause decreases in mental and physical health. Based on a detailed literature assessment, we report strong evidence of positive relationships between exposure to nature and a broad range of human health and well-being measures, and more limited but intriguing information indicating that biodiversity exposure also can improve health. This information provides additional rationale to support protection and restoration of healthy ecosystems and biodiversity. Restoring and conserving natural characteristics of the Gulf ecosystem, including biodiversity, would enhance community resilience and promote important health benefits that may be conferred by simple exposure to nature and biodiversity. Accomplishing this will require new research and policy strategies involving transdisciplinary collaboration among ecological, environmental health, biomedical, and conservation scientists as well as urban, land and coastal planners and private business.

Translating Lessons from the Gulf Oil Spill into Improved Disaster Health Research

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Progress in disaster preparedness, response, and recovery of the affected communities is hampered by the relative absence of scientific data to understand the longer-term health effects, community resiliency, and efficacy of our public health measures. The unique National Institute of Environmental Health Sciences' (NIEHS) response to the Gulf Oil Spill disaster, which included research of 32,000 spill clean-up workers, an extramural community-academic research consortia, and worker education and training efforts, can serve as a framework for discussing the challenges of performing timely disaster research. NIH efforts are being undertaken to improve the collective capability to perform needed health and scientific research to address longitudinal questions and concerns. The NIEHS, in collaboration with the National Library of Medicine (NLM), has embarked on a NIH Disaster Research Response (DR2) Project, a pilot program designed to create new infrastructure and approaches to help overcome current barriers to disaster research. The elements of the proposed research system include: pre-approved research protocols; web-based toolkit consisting of questionnaires, training materials, and manuals to support data and biological sample collection; and the creation of a national network of trained environmental health researchers working in collaboration with community partners to jointly conduct needed research, and harness our evolving "citizen science" platforms. This session will discuss key components of the new NIH DR2 Project and our efforts to facilitate an effective national network for performing timely environmental health research in a disaster setting.

Approach for Improved Public Health Guidance for Beach Use during and after Oil Spills

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With increases in Gulf oil drilling since the 1940s, the U.S. coastal beaches have experienced a series of catastrophic ecological events which resulted in devastating impacts on recreational beach use. In the aftermath of the Deepwater Horizon (DWH) explosion in 2010, not only have people made choices to

avoid the Gulf Coast beaches but also avoid beaches far beyond the impacted areas and beyond the duration of the spill. There is a need to understand why these choices were made in an effort to develop more effective risk communication strategies with more timely risk assessments and delivery of educational outreach that empower individuals to make appropriate decisions. The authors propose a Public Health Guidance System (PHGS) which serves to optimize human decision-making associated with oil spills through improved estimates of health risks and communication of this risk to encourage beach use and minimize negative health outcomes. Risk assessments for beaches impacted by oil spills would benefit from improved measures of microbial risks from oil spills (in addition to the chemical risks), and from quantifying human behaviors that may contribute to exposures. Risk communication would benefit from research in understanding how individuals make decisions during situations of uncertain environmental health threats, in particular during and after oil spills. In all cases the science should be translated into materials that can be easily understood with outreach to the primary key stakeholder group, Gulf and beach user population, directly through traditional and electronic means. This presentation will provide the framework for the PHGS which integrates science and community awareness in a fashion that will optimize decision-making.

The Gulf Research Program - Strategic Vision and Initial Activities

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The National Academy of Sciences (NAS) is an independent, non-profit organization chartered by Congress in 1863 to provide expert scientific, engineering, and health advice to the nation. In 2013, as part of the criminal plea agreements with the companies held responsible for the Deepwater Horizon explosion and fire, the courts asked the NAS to form and administer a $500 million, 30-year program focused on oil system safety and the protection of human health and environmental resources. The Gulf Research Program seeks to bring the best expertise in science, engineering, technology, and health to advance understanding of the Gulf of Mexico and use that information to help prevent offshore disasters, minimize adverse impacts of offshore energy production, and ensure that the ecosystem and surrounding human communities are resilient to shocks and long term changes. The Program will encourage cross-boundary work across disciplines, across geographic borders, and across perspectives and will fund activities in three categories: research and development, education and training, and environmental monitoring. This presentation will review key elements of the Program's strategic plan (released September 2014), including mission, goals, objectives, and initial activities for 2015 and 2016.

Cultural Differences across Disaster Resilient Communities

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The Transdisciplinary Research Consortium for Gulf Resilience on Women's Health (GROWH) was created to examine the potential adverse health effects in pregnant women and women of reproductive age in the aftermath of the Gulf of Mexico Oil spill. The GROWH community- academic partnership included an innovative use of locally-trained community health workers to explore the specific role culture plays in community resilience. The study involved first-time mothers (n=124) across several Southeast Louisiana parishes to examine their cultural beliefs regarding hurricane threats and associated risk behavior. Cultural consensus analysis then quantified cultural agreement, and estimated a

culturally-correct answer key. Preliminary results showed that women living in parishes of lower community resiliency were 5.75 (CI 1.23-26.86) more likely to be in a subculture holding heightened hurricane risk perceptions and risk behaviors. Stark differences were present throughout the cultural perceptions of women according to the measured resiliency of their parish. Cultural consensus analysis offers an accessible tool to incorporate direct measurement of cultural beliefs in traditional environmental disaster research. Comparing cultural beliefs between communities of varying resiliency will help to uncover upstream determinants of disaster recovery, while strengthening culturally-tailored, effective post-disaster environmental health interventions in at-risk populations.

Building Responder Resilience and Reducing Mental Health Consequences during Disasters through Training; Final Outcome Reports

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As in prior major disasters, data collected after the Deepwater Horizon oil spill disaster indicate a significant mental health component to the health consequences of the event. Workers exposed to oil, who lost income due to the spill and who had experienced repeated disasters were found to have a higher rates of stress, anxiety, depression and PTSD. Impacted Gulf Coast communities have limited access to behavioral health services and negative health effects are still seen today. With an understanding of the problem, and to better assess the solutions to mental health concerns for workers during response to disasters, the NIEHS Worker Training Program, partnered with the Substance Abuse and Mental Health Services Administration (SAMHSA), to create the Gulf Responder Resilience Training Program. Through this program, NIEHS held meetings with medical providers, mental health practitioners, community groups and academia to better understand resources and needs. It was determined that workers and their supervisors, often impacted community members themselves, are a high risk population that could benefit. Training materials for both populations have been developed and pilot tested. The four hour training program uses activities and interaction to engage participants in discussion and begin building long term capacity for mental health and resilience. The development, implementation, and outcomes of this innovative new program, will be reviewed and future steps explored.

Oil Spill Community Engagement: Transdisciplinary Lessons to Support Community Resilience

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Oil spills can impact communities' way of life, culture, and income. This presentation discusses findings of inter-related research projects that examined ways to think ahead about and assess oil spill risk and response perceptions and options at the community level. These projects, conducted following the 2010 Deepwater Horizon incident, reviewed prior research and practice on community engagement with regard to oil spills, and engaged stakeholders at the community level through interactive oil spill preparedness and response workshops. The workshops assessed and addressed oil spill risk and response perceptions with an interactive mental models survey tool, and built relationships between responders and others in the communities with science café-style interactions. Findings from this work

provide insights into community-level risk perceptions about oil spills and response options, as well as opportunities for improved risk communication which if implemented would contribute to adaptive community resilience from oil spill disasters going forward.

Developing an Applied Community Based Participatory Research Curriculum Tailored to Gulf Cost Communities in Louisiana

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The Transdisciplinary Research Consortium for Gulf Resilience on Women's Health (GROWH) addresses health disparities in the Gulf Coast by linking communities and scientists through community engaged research. Funded by NIEHS, GROWH's Community Outreach and Dissemination Core (CODC) seeks to utilize Community Based Participatory Research (CBPR) and other community centered outreach strategies to strengthen community resilience in vulnerable Gulf Coast populations. The CODC is an academic-community partnership comprised of Tulane University, Mary Queen of Vietnam CDC, Bayou Interfaith Shared Community Organizing, and the Louisiana Public Health Institute. In response to feedback from community partners, the CODC collaboratively developed an innovative 6 session curriculum designed to impart applied, practical knowledge to community based organizations and academic researchers on the successful formulation, execution and sustaining of CBPR partnerships. The curriculum is tailored to the context and needs of the GROWH CODC partners, and will produce measurable deliverables upon completion. Preliminary findings from the pilot sessions and rigorous evaluation activities will be presented, as well as examples of materials developed for the curriculum. CBPR holds strong potential for environmental health research, and both community and academic partners must be able to effectively apply CBPR methods and approaches in order for CBPR projects to successfully address health disparities.

The Value of Transdisciplinary Research Integrating Public Health and Ecosystem Services Research

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It is exciting and daunting to review the reports in this Session and throughout the GOMRI meeting describing what we have learned about the health and ecological implications of the Deepwater Horizon oil spill. Exciting because so much has been done, daunting because we realize we have barely scratched the surface of what we need to know to be responsive to the public's concerns about the short and long term effects of the spill. In this Session we will review existing public health and ecosystem services transdisciplinary research related to the oil spill; examine its relevance to the health and well-being of coastal communities; and discuss its translation into effective community- based practice. What is very clear is the value of transdisciplinary research that integrates ecosystem services, social and behavioral sciences, and public health - and that links resilience and risk reduction. Hanging over our heads is the imperative to learn as much as we can from the DWH incident so as to be prepared for the next oil spill or similar disaster. For such transdisciplinary research to be successful in the short term requires cooperation among academic disciplines and enlistment of the support and participation of communities, governmental agencies and other stakeholders. But research into improving community and ecosystem resilience is a longer term activity which must persist beyond the immediate recollection

of the disaster. For this to occur, education at all levels is crucial. We must not go back to the complacency of the past.

Session 006
Emerging Ecological Impacts of the Deepwater Horizon Oil Spill: Evaluating Ecosystem Change and Resiliency

Reef Fishes and the Deepwater Horizon Oil Spill: Chronic Effects and Evidence of System Resiliency

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Lessons from past large-scale oil spills suggest that chronic impacts on ecosystem services may not be apparent for years following a given spill, but also that the existence of pre-spill baseline data is critical for evaluating acute as well as chronic impacts. Reef fishes have been examined as indicator species of ecological impacts of the DWH in the nGOM due to extensive pre-spill data on their community structure, feeding ecology, and population dynamics, as well as the fact that movement behavior ranges from site-attached to migratory among species. Liver PAH concentrations and enzyme activities clearly indicate that reef fishes were exposed to petroleum hydrocarbons in the weeks to months following the DWH spill, although exact mechanisms of exposure remain unclear. Acute impacts include declines in reef fish numbers and biomass on natural and artificial reefs across the nGOM shelf in a study region from approximately 86.25W to 88.25W, with the most severe declines observed in small demersal fishes, such as damselfishes, cardinalfishes, and wrasses. Chronic effects include food web impacts, dietary shifts, and lower growth rates in the years following the spill. By the fourth year post-DWH, fish communities were showing signs of resiliency. An exception to that trend is the persistence of lower densities of small demersal fishes, which is confounded by the exponential increase in invasive lionfish densities in the system. Furthermore, evidence from stable isotope analysis of reef fish muscle tissue indicates food web effects of the spill persisted at least into 2014. Trends observed in reef fish ecological parameters will be examined in the context of chronic effects of the spill and the potential for diminished ecosystem services.

Resilience in the Northern Gulf of Mexico Offshore Plankton Community

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Eutrophication, trophic cascades due to overfishing, and the Deepwater Horizon (DWH) oil spill have impacted the plankton community in the northeastern Gulf of Mexico (NE GOM). Seasonal phytoplankton and zooplankton distributions collected between August 2010 and August 2013 were used to assess resilience of the plankton community to the DWH oil spill. Interannual plankton dynamics in this region are strongly driven by seasonal changes in nutrient-rich riverine outflow. August 2010 and 2013 had the highest plankton concentrations coincident with high river flow, while September 2011 and August 2012 had significantly lower plankton concentrations associated with relatively low river

outflow. Despite the interannual changes in abundances, biodiversity indices and percent composition of dominant taxa were similar between years. A notable difference was that the dominant copepod species changed at near-shore sites between years. Marine snow concentrations also were high (>60,000 particles/m3) in regions associated with riverine outflow and contributed to the flux of oil to the seafloor. A better understanding of the role of riverine influences on marine production and particle sedimentation is needed to predict the impact of oil spills, as most deep-water oil exploration worldwide occurs near deltaic systems. A full assessment of ecosystem resilience is hampered by the lack of pre-spill data. Future work includes analyzing NOAA/NMFS bongo net samples to establish a pre-spill baseline.

Condition, Diet, and Growth of Larval Spanish Mackerel (*Scomberomorus maculatus*) in relation to the Deepwater Horizon Oil Spill

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The Deepwater Horizon oil spill (DWHOS) coincided temporally and spatially with the pelagic early life stages of many fishes in the northern Gulf of Mexico. Using samples from a long-term ichthyoplankton survey off the coast of Alabama, we seek to resolve the effects of the DWHOS on larval fishes. We compared the condition, growth, and diet of Spanish mackerel (*Scomberomorus maculatus*), collected during summer months in years before (2007-2009), during (2010) and after (2011-2013) the DWHOS. Comparisons of condition using morphometric analyses and weight-length relationships revealed that larvae were deeper-bodied and heavier during the DWHOS period, relative to pre- and post-spill periods. Additionally, larvae in June and July were in better condition than larvae in May across all years. Preliminary results indicate the most abundant prey items of larval Spanish mackerel were larval fish, copepods and ostracods, however diet composition did not differ among the three time periods. Also, results suggest daily growth did not differ between larvae collected during and after the DWHOS (no pre-spill otoliths were available for analysis). Overall, our results show that larval Spanish mackerel may have been resilient to harmful effects of the DWHOS. Potential impacts of the DWHOS on larval fishes, however, may be species-specific, and future research will include analyses of other scombrids, as well as species from other families, to examine broad taxonomic patterns.

What Have We Learned About the Oceanic Fish Fauna of the Gulf of Mexico? Initial Results of the NOAA Offshore Nekton Sampling and Analysis Program

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The Deepwater Horizon Oil Spill (DWHOS) necessitated a whole-water-column approach for assessment that included the epipelagic (0-200m), mesopelagic (200-1000m) and bathypelagic (>1000m) biomes. The latter two biomes collectively form the largest integrated habitat in the GoM. This habitat received the initial oil/methane discharge, plus millions of liters of dispersant, and contained persistent deep (~1100m) plumes of oil and dispersant. By some estimates, only half of the discharged oil and none of the methane reached the ocean surface, demonstrating that DWHOS had an extensive deep-pelagic component. Before the DWHOS we had only a basic knowledge of the deep-pelagic GoM. Data

regarding biodiversity, abundance, and distribution of the pelagic fauna were not comprehensive and thus, a large-scale program, the NOAA Offshore Nekton Sampling and Analysis Program (ONSAP), was implemented as part of the NRDA process. Here we provide the initial results of a 3-month ONSAP field campaign in 2011 in which the pelagic fauna was sampled from 0-1500 m. During this campaign, from the 87,402 specimens collected, a minimum total of 459 fish species were represented. Ongoing analyses will certainly increase this number, as hard-to-identify taxa are resolved. This figure represents nearly one-third of the fish species currently known for the GoM. Of these species, 53 are previously unknown in the GoM, including previously undescribed species.

The Forgotten Habitat, Modeling Pelagic Species and Ecosystem Response to DWH in the Offshore Waters of the Gulf of Mexico

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The Deepwater Horizon (DWH) incident coincided with the spring spawning season of Atlantic bluefin tuna (BFT) in the northern Gulf of Mexico (GOM). Atlantic bluefin were one of the pelagic species of immediate concern to NOAA as the spill began during the spawning season, and the Gulf of Mexico is the primary spawning grounds for the western Atlantic stock. In order to assess the impact on larval bluefin habitat we applied a newly developed neural network habitat model trained with archival data extending back to 1982. As a result, NOAA was able to quickly estimate that the impact on bluefin was not severe enough to close the entire Gulf of Mexico to long-lining. This model has undergone continued development which includes new sampling methods, refining the environmental relationships, and modeling the source of the larvae through backtracking techniques to better define bluefin spawning habitat. Recent analysis also suggests convergence zones and Lagrangian Coherent Structures may play a role in aggregating bluefin larvae, and needs to be taken into account when assessing impacts to the ecosystem. These techniques can and should be applied to other species and to develop predictive tools for larval and adult habitats focused on identifying change over time and each habitat's ability to withstand and recover from future natural or anthropogenic impacts to the ecosystem.

Larval Fish Assemblages Associated with Mesoscale Structures of the Deepwater Region of Mexico's EEZ: A Post-Oil Spill Baseline Study

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Evaluation of oil spill impacts requires baseline data encompassing a variety of scales and oceanographic processes. The GM circulation patterns and hydrographic characteristics are heavily influenced by mesoscale structures. Coupled with reproductive behavior, circulation patterns influence larval fish dispersion and assemblages, and the susceptibility of specific taxa and regions to oil spills. We characterized the larval fish assemblages associated with specific mesoscale features of the deepwater region of the central GM during November 2010 (fall) and July 2011 (summer). We hypothesized there would be greater taxonomic similarity between stations associated with a given structure. Four structures with contrasting hydrographic characteristics were identified based on AVISO altimetry and analysis of CTD profiles: region of influence of the Loop Current (LC), anticyclonic gyres that spun off the

Loop Current (ACG-LC), the semi-permanent cyclonic gyre of the western Bay of Campeche (CG-BC) and the near-platform region of the BC (NP-BC). Although the number of taxa did not differ between structures, there was a higher diversity in stations within the influence of the LC. Stations corresponding to LC and ACG-LC were dominated by meso- and bathypelagic taxa, while those from CG-BC and NP-BC had a mix of coastal and mesopelagic taxa. Cluster analysis indicated a high similarity between many of the stations of the LC and ACG-LC (north-central gulf) as well as those within BC, possibly indicating the presence of two regional assemblages driven by large-scale reproductive and circulation patterns. Nevertheless, some stations had a very low level of similarity, which may be indicative of the importance of smaller-scale processes.

Vulnerability of Fish Larvae Populations to an Oil Well Blow Out in the Gulf of Mexico

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After the Deepwater Horizon (DWH) blowout on April 20th, 2010, an estimated 4.9 million barrels +/- 10% were released into the Gulf of Mexico over 84 days. After this blowout, there was a need to determine which species and quantities of fish had been exposed to the oil. This study will evaluate, across numerous taxa, the proportions of fish larvae by species or genus that were located within the spatial domain of the spill. Many economically important fish species spawn in northern Gulf of Mexico waters in the vicinity of the DWH oil spill within the temporal extent of the DWH oil spill (April through July). Differing spatial distributions of larvae due to different spawning locations and seasons predict that species were disproportionately affected by the DWH spill. In this study, ichthyoplankton data collected during the Southeast Area Monitoring and Assessment Program - Gulf of Mexico (SEAMAP) during years 1982-2010 was used to estimate the proportions of individual species of larval fish that were exposed to DWH oil. These seasonal plankton surveys span the northern part of the Gulf of Mexico and record ocean physical characteristics as well as the abundance at various taxonomic levels in the top 200 m of depth. Generalized additive models (GAMs) were built to predict the location and abundance of various species of ichthyoplankton in the Gulf of Mexico given a time of year and environmental variables. This model combined with the wide spatial distribution of the SEAMAP samples has important utility in predicting the impacts of spills virtually anywhere in the Gulf of Mexico and will allow for computation of the intersection of any spill trajectory for any length of time with the modeled ichthyoplankton data.

Taxon-specific Variability in Condition among Larval Fishes Collected before, during, and after the Deepwater Horizon Oil Spill

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Variability in fish recruitment to adult populations is largely related to variability in survival during early life. In addition to direct mortality (e.g., toxicity), the release of oil and application of dispersant after the Deepwater Horizon oil spill (DWHOS) may have impacted larval fish survival by disrupting planktonic food webs. We measured proxies for condition (morphometrics and dry weight, standardized by length)

for Red Snapper, Spanish Mackerel, and Atlantic Bumper larvae collected during summer months in years prior to (2007-2009), during (2010) and after (2011-2013) the DWHOS. Within each period (pre-, during and post-spill), condition generally increased for each species during the summer, which suggests a seasonal pattern in condition common across taxa. However, the overall pattern among periods differed by species. Relative to pre- and post-spill periods, Spanish Mackerel larvae were in better condition during 2010, whereas Red Snapper larvae were in poorer condition. There was no significant difference in the condition of Atlantic Bumper larvae among the three periods. Our analyses of zooplankton suggest many potential larval fish prey were abundant, and assemblages were largely resilient to DWHOS impacts. Further research will include comparative diet and growth analyses in an attempt to resolve these observed patterns in larval fish condition. Our results clearly indicate that taxon-specific responses need to be examined during all life stages.

The Interaction between Benthic Bioturbators and Microbes on the Fate of Hydrocarbons in Sediment - 1) Sediment Characteristics and PAH Levels

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Bioturbators rearrange large amounts of sediment and modify sediment characteristics. When an oil spill introduces hydrocarbons into the sediment, the presence of bioturbators' burrows can facilitate sediment penetration into the sediment and their bioturbation may move the contaminated sediment. Bioturbators may also modify various sediment characteristics (redox potential, oxygen levels, organic content, etc.) that can affect microbial abundance, activity and community composition. This can in turn lead to changes in the microbial community's capacity to break down oil. We are performing experiments to determine the effects of bioturbators on the distribution and degradation of hydrocarbons. The experiments use beach sediment, seawater, bioturbators (the ghost shrimp *Lepidophthalamus louisianensis* and the razor clam *Tagelus plebeius*), in greenhouse mesocosms dosed with surrogate oil. Water column and sediment characteristics (incl. PAH levels) are monitored, along with the microbial community and its capacity to break down phenanthrene. Results to date indicate that the bioturbators do indeed affect both the mesocosms' environmental conditions (such as sediment redox values) and the fate of the hydrocarbons (as seen in an increased loss of PAH from surface sediment), with the effects appearing more pronounced for ghost shrimp than for razor clams. The microbial aspects will be covered in a separate presentation.

The Interaction between Benthic Bioturbators and Microbes on the Fate of Hydrocarbons in Sediment - 2) Microbial Composition and PAH Degradation

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Ghost shrimp and razor clams are widely distributed in the intertidal to subtidal zones of the Gulf of Mexico, therefore, it is very important to understand their role in hydrocarbon removal after the spill through activation of the sediment microbial community by bioturbation. A greenhouse mesocosm experiment was set up in which ghost shrimp and razor clams were used as bioturbating agents. The microbial community changes were followed by 16S rRNA gene sequencing and the rates of PAH degradation were determined using mesocosm sediment spiked with radiolabeled naphthalene. The data suggests that the sediments, especially the bioturbated sediments, which were previously exposed

to oil, have significantly higher oil degradation rates than oil-free sediments. The effect of the ghost shrimp bioturbation was particularly prominent: naphthalene degradation rates increased three-fold in sediment from ghost shrimp mesocosms. The bioturbation mediated by razor clams did not significantly increase naphthalene degradation rates. Bioturbation alone (without oil activation of the microbial community) did not show any significant effect on the naphthalene degradation rates. No significant changes were observed in the bacterial community composition on the domain level following oil augmentation whether or not a bioturbator was present, though ongoing analyses at lower taxonomic levels seem to indicate alterations in the microbial community.

Megainvertebrate Communities Resiliency to IXTOC-1 Oil Well Blowout

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During 1979-1980 Ixtoc-1 oil well blowout poured thousands of tons of oil in the Southwestern Gulf of Mexico that highly impacted the ecosystem. Studies on benthic megainvertebrates in the Campeche Sound were systematically done along the 1984-2010 period. In the initial sampling (1984), ordination analysis based on abundance data of crustaceans, mollusks, and echinoderms revealed four main assemblages which seem to be mainly determined by depth and sediment type. The community structure was relatively constant along the period studied, the observed variations in diversity and abundance values were not directly related with oil hydrocarbons. Decreasing abundance was remarkably evident in exploited species like white and pink shrimp that collapsed to about a 10% of its population size. Since 1979, the benthic communities in the SWGoM have been subjected to a chronic exposure of oil hydrocarbons industry and also probably favored by a “shelter” effect of an “exclusion zone” (4000 km2) closed to fishing and navigation. White and pink shrimp population did not exhibit any positive impacts related with the closed area, on the contrary they presented decreasing trends in population size, larval abundance, recruitment levels and reduced offshore distribution. Stock Recruitment relationships of both shrimp indicate that they have a high recovery potential. Growth and recruitment overfishing rather than Ixtoc-1 blowout and/or chronical pollution are more likely responsible of shrimp population collapse. Data showed a high ecosystem resiliency where fishing effort seems to be the most important stressor.

A Generalized Additive Model Predicting Abundance of Pelagic Species within the Gulf of Mexico

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There are growing concerns for the sustainability of pelagic species in marine ecosystems around the world, including the Gulf of Mexico. Knowing the spatial areas where organisms congregate - making them more vulnerable to fishing pressure - could inform conservation efforts. We used generalized additive modeling (GAM) to compute spatial abundance estimates for approximately 25 species within the Gulf of Mexico using catch and effort data from the longline observer program. Model predictors included sea surface temperature, bottom depth, sea surface height, and loop current position. To account for the catch data’s zero-inflated nature, binomial GAMs were used to predict catch presence/absence and Gaussian GAMs predicted abundance using log-transformed catch. Catch data were split into testing and training datasets to compare predicted and observed values. The model

works better for some species (e.g., *Xiphias gladius*) than others (e.g, *Galeocerdo cuvier*) because not all pelagic species distributions are correlated with environmental variables considered here. Future work will involve incorporating other environmental variables into the statistical models (e.g., dissolved oxygen), as well as improving the quality of the data. The results from this work will be used to inform the Gulf of Mexico Atlantis model, a spatially explicit ecosystem model. Atlantis allows the investigation of various ecosystem impacts to the Gulf of Mexico due to changes in fisheries management or environmental conditions (e.g., the Deepwater Horizon oil spill).

Evaluation of Multiple Stressors in Combination with Oil using *Fundulus grandis*

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The 2010 Deepwater Horizon oil spill resulted in the release of ~ 5 million barrels of crude oil from the Macondo wellhead into the Gulf of Mexico. In addition to the anthropogenic-induced stress of polycyclic aromatic hydrocarbon (PAH) exposure, aquatic organisms living in estuarial areas of the Gulf of Mexico must also contend with environmental stressors including large fluctuations in dissolved oxygen (DO), temperature, and salinity. For this study, *Fundulus grandis* was chosen as a model species to investigate the combined effects of PAHs and environmental stressors. Embryos <24 hpf were exposed to various PAH concentrations and environmental conditions (DO: 2, 7 ppm; temperature: 20, 25, 30°C; salinity: 3, 7, 30 ppt) until hatching and concentrations eliciting 50% mortality (LC50) calculated. Regardless of environmental conditions, LC50 values fell within a narrow range (43.2- 60.9 ppb), with the exception of one experiment conducted at low temperature (20°C) and high salinity (30 ppt) resulting in an LC50 value of 184.4 ppb. The data suggest that environmental parameters such as salinity and temperature that are known to vary widely in the northern Gulf of Mexico can affect the acute toxicity of PAHs during early life stage development. The results of this study may be used to construct population models for *F. grandis* and other teleosts based on environmental conditions and oiling known to exist in the Gulf of Mexico.

Using Acrobat Ants to Determine the Effect of Macondo Oil on Saltmarsh Terrestrial Arthropod Food Webs

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Acrobat ants, *Crematogaster pilosa*, form colonies inside hollow stems of the dominant plant, *Spartina alterniflora* in marshes of northern Gulf of Mexico. These omnivorous ants are great indicators of cascading effects of environmental stress, but were undiscovered until our study. Therefore, we used them to tease out trophic effects of oil and catastrophic storms. We marked ant colonies, identified food sources, documented mating flights and new colonies, and followed colonies for >5yrs. Simultaneously on the same plots, we collected terrestrial arthropods. In 2010, ants were suppressed 30% in oiled marshes compared to reference plots. By 2011, the arthropods available for ants to eat declined, and ant populations fell in oiled marshes. Tropical storm Lee surged >30hr over the ant plots; we found ant populations did not differ. In 2012, mated queens flew into and populated oiled marshes in spring, but those colonies died in July 2012, presumably because of lack of food; new colonies in reference marshes survived. On Aug 29, 2012 Hurricane Isaac surged >62hr over the ant plots. In early 2013, populations of

ants in all areas (oiled and reference) were suppressed by >98% due to Isaac. In early summer 2013, ant populations began to recover in both oiled and unoiled areas, but died in oiled plots by October 2013. However, during 2014, arthropods repopulated oiled areas and in Sept 2014, although still significantly suppressed, ant populations in oiled areas appear to be resurging.

Stable Isotopes in Fish Eye Lenses as Potential Recorders of Trophic and Geographic History

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Oil-spill impacts on fish cannot be studied without first understanding site fidelity and movement. Previously, there have been no known long-term records of $\delta^{13}C$ and $\delta^{15}N$ isotopes in bony fish. We evaluated eye lenses as potential recorders of isotope histories because the hardened inner lens (lens nucleus and inner cortex) consists of metabolically inert optical proteins deposited in successive, concentric layers, much like the layers of an onion. These layers ("laminae") can be readily dissected for isotopic analysis. We conducted four tests on lenses from Red Snapper, Red Grouper, Gag, and White Grunt. Low-resolution screening (groups of laminae) exhibited substantial $\delta^{13}C$ and $\delta^{15}N$ isotopic variability, while high-resolution temporal analysis (individual laminae) revealed additional early-life details. The third test compared left- and right-eye variation, revealing almost identical isotopic patterns. The final test evaluated intra-laminar variation by analyzing multiple samples from different parts of the same lamina, using three individuals of two species. Variations among laminae were found to be much higher than variations within laminae for both $\delta^{13}C$ [$F(6,16) = 40.6$, $p < 0.0001$] and $\delta^{15}N$ [$F(6,16) = 232.4$, $p < 0.0001$]. Eye lens isotopes appear to be useful for reconstructing the isotopic histories of individual fish; these histories can be compared with spatially derived isoscapes to reconstruct individual histories for site fidelity, movement, and trophic position.

Impact of the Deepwater Horizon Incident on Planktonic Ecosystems: Carbon is Important, But So Is Nitrogen!

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The Deepwater Horizon (DWH) incident in 2010 discharged an unprecedented volume of oil and gas into pelagic waters of the Northern Gulf of Mexico. This perturbation of the pelagic carbon cycle had a rapid and clear impact on microbial communities, altering the composition and activity of both pelagic and benthic microbes, but its impact on critical elemental cycles is less clear. In most marine systems, nitrogen availability limits biological production, creating a tight connection between the oceanic carbon and nitrogen cycles. We explored these connections during a series of cruises to the Northern Gulf of Mexico beginning shortly after the Deepwater Horizon spill and continuing at roughly 1 year intervals. We carried out a series of nutrient amendment (N, P, Si) experiments to test the controls on phytoplankton growth in areas affected by oil and gas release. Our amendments showed a clear response to N, and sometimes N+P additions, implying widespread N limitation of production in the Gulf. On each cruise, we also measured the rates of C- and N-fixation in surface and deep waters, and measured the rate of CH4 assimilation at depth beginning in 2013. Immediately after the DWH incident, we found elevated rates of N2-fixation in subsurface waters that generally exceeded the substantial

rates of N2-fixation occurring at the surface. In subsequent years, we found elevated rates of N2-fixation at depth only in the vicinity of natural seeps, suggesting that the time scale of biogeochemical recovery from the DWH incident was on the order of a year.

A Correlation of Vitellogenin and Polycyclic Aromatic Hydrocarbons in Red Snapper and Golden Tilefish Exposed to the Deepwater Horizon Oil Spill

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Environmental contaminants, such as polycyclic aromatic hydrocarbons (PAHs), can disrupt the endocrine system and alter reproductive function of wildlife. They are known to adversely affect survival, growth, and reproduction in many aquatic species and due to the significant input from the Deepwater Horizon oil spill, they may radically impact fish exposed during the spill. Vitellogenin (VTG) is an egg-yolk precursor protein expressed in the females of nearly all oviparous species and is commonly used to detect estrogenic effects in male fish. Plasma concentrations of VTG in males and juvenile fish or elevated VTG levels in mature females is an indication of xenoestrogens in the aquatic environment. Assays for vitellogenin, were performed on red snapper (*Lutjanus campechanus*) and golden tilefish (*Lopholatilus chamaeleonticeps*) plasma collected from areas in the Gulf of Mexico including areas near the Deepwater Horizon blowout, using a rainbow trout ELISA based sandwich assay. Circulating plasma concentrations of VTG in males and juvenile fish or elevated VTG levels in mature females is an indication of xenoestrogens in the aquatic environment. Concentrations ranged from 0.00-512.76 ng/ml in golden tile fish females and 0.00-97.96 ng/ml in males. For red snapper, the concentrations were less and ranged from 14.26-318.45 ng/ml in females and 6.86-27.20 ng/ml in males. All vitellogenin data were compared to bile PAH metabolite and PAH surface sediment concentrations.

Cytokine Expression Patterns in Red Snapper and Golden Tilefish Collected from the vVcinity of the Deepwater Horizon Oil Spill in 2013-2014

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Exposure to crude oil can alter the immune response of fish, rendering them susceptible to disease. Although the mechanism and magnitude of oil toxicity has not been fully described, modification of cytokine expression may be a governing factor. Cytokines are pleiotropic signaling proteins, with pro- and anti-inflammatory roles. While recent work demonstrates cytokine modulation upon exposure to crude oil in select species, their expression behavior in red snapper and golden tilefish has not been studied. Four cytokines, IL-1β, IL-8, IL-10, and TNFα, were cloned and characterized from these fish for the first time. Their sequences shared high homology with other Perciformes and are being utilized to create the first multiplexed Perciform-specific kit for cytokine detection. This will be correlated with in situ and in vitro gene expression studies. Tissue and whole blood samples were collected in the vicinity of the Deepwater Horizon oil spill in 2013-2014. Cytokine gene expression was measured in the samples using quantitative real-time PCR to establish species differences, spatial disparities among fish, and matrix expression patterns within individuals. Future work includes establishment of snapper spleen cultures and challenges with Deepwater Horizon crude and Corexit 9500 to assess cytokine gene

expression change in vitro over a 96-hour period. This work will enhance our understanding of teleost cytokine expression in relation to oil contamination events.

Post Exposure, Sub-lethal Effects of Oil Exposure on Bay Anchovy (*Anchoa mitchilli*) Larvae

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Bay anchovy (*Anchoa mitchilli*) is an ecologically important forage fish in the Gulf of Mexico. They are prolific spring and summer spawners, with abundant planktonic larvae that likely encountered oil during the DWH spill at both lethal and sub-lethal concentrations. In an effort to compare responses among different life stages and to assess long-term impacts on growth, larvae were exposed to both high and low energy water-accommodated fraction (WAF) of Macondo surrogate oil, chemically-enhanced WAF (CEWAF), and dispersant (Corexit9500) at multiple life-stages for 24 hours. No mortality was induced by low-energy WAF (LEWAF) exposure, but mechanically dispersed (high-energy WAF; HEWAF) and chemically dispersed (CEWAF) oil and Corexit9500 induced differential mortality among the life stages. Additionally, first-feeding bay anchovy were exposed for 24 hours to two sub-lethal concentrations of CEWAF and transferred to clean seawater where they were allowed to grow for 6 days in two separate trials. Both trials resulted in limited mortality after 24 hours, but significant and dose-dependent mortality occurred during the 6 day growth period. Further, exposed animals displayed reduced growth in weight following initial exposure to CEWAF in separate trials. These results show that bay anchovy are most sensitive to oil as newly hatched larvae and that early, sub-lethal exposure can impact growth, and therefore fitness, of larvae in response to exposure to oil.

Impacts of a Marine Gas Well Blowout on PAH Contamination in Sediments and Fish

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On July 23, 2013 a marine gas well (Hercules #265) began leaking and subsequently ignited in the northern Gulf of Mexico. The well fire burned out of control for several days before being extinguished. As there were considerable data from studies associated with the Deepwater Horizon incident, we sampled near Hercules 265 after the fire to ascertain if sediments and fishes were polluted by the blowout. A surface drifter study conducted in late July-early August, 2013 confirmed water flow generally SE of the Hercules 265 site. We sampled sediment cores at ~200 m, 8 km and 18 km SE from the well using a multicorer, and set a longline (508 hooks) from ~200 m to 9 km SE the well to catch fishes. In sediment, profiles of LMW PAHs showed no clear trend with distance from the well. In contrast, HMW PAHs showed a spatial trend of decreasing concentrations for recently deposited surface sediments (< 6 mm). Among the most abundant carcinogenic PAHs is benzo[a]pyrene. For fish, florescent aromatic compounds in bile were determined for 22 red snapper. There was no decline in the concentration of metabolites in red snapper with distance from the well. However, mean benzo[a]pyrene metabolite concentrations were nearly double those from 2012 ($P<0.01$). Both surface

sediment and fish bile analyses, reflecting the most recent exposure, indicate increased abundance of pyrogenically-derived hydrocarbons, possibly from Hercules 265.

Atlantis Ecosystem Modelling of the DWH Oil Spill

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We present a spatial biogeochemical model of the Gulf of Mexico marine ecosystem developed for the CIMAGE consortium. The model was developed to examine ecosystem-scale impacts of the Deepwater Horizon oil spill and forecast recovery time across a wide range of species. Model training uses a historical reconstruction from 1980 to 2010 driven by time series of catch and spatial-temporal fishing closures and restrictions. Forecasts from 2010 to 2030 include oil spill effects. Oil spill effects are modelled using spatial forcing functions on growth, mortality and recruitment for about 20 fish functional groups. Functional relationships relate the concentration of oil (from far-field modelling) to growth and mortality effects. The functional relationships are based on laboratory work in the CIMAGE project and a review of earlier oil spill literature. Further, recruitment effects are estimated using an individual based model of larval transport, where contact with oil is assumed to result in larva death. Diagnostic simulations are presented to demonstrate model behaviour. Early results on spatial oil forcing are presented. Potential validation strategies are discussed that would take advantage of CIMAGE ichthyoplankton survey data and reef fish community survey data.

Ecosystem Modeling: An Approach to Estimate Effects of PAH on Fishes

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Creation of new subroutines in the Atlantis modeling software now allows for the alteration of a functional group's growth, recruitment, and mortality across space and time. These new forcing functions will be used to model possible ecosystem shifts in the Gulf of Mexico related to the Deepwater Horizon oil spill. To understand how growth and mortality might have changed, a comparative analysis was done between physiological data of fish captured after the spill and the predicted cumulative oil exposure level of the capture site. Due to limited available data sets relating to the Gulf oil spill, a literature search was done to examine impacts on fishes from oil exposure. The majority of oil exposure literature found was qualitative in nature, so the search was expanded to polycyclic aromatic hydrocarbon (PAH) exposure studies. An AIC was used on the combined data to determine the relationship that best describes the correlation between exposure level and impact on growth and mortality. Using the best fit model, a field of relative impact for the Gulf of Mexico can be created for these two dynamics. This oil affected population relationship will be implemented into the new forcing function subroutine, and simulations run to determine possible ecosystem effects.

Session 007
Making a Living on Hydrocarbons: Diversity, Metabolic Potential, and Regulation of Microbial Hydrocarbon Oxidation

Preparedness for a Major Deepwater Spill in the Northeast Atlantic, and Uncovering Novel Oil-Degraders in the Ocean

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The main agents of oil removal in the sea are microorganisms, yet a major problem we face in studying the impact of oil contamination in the ocean is that we often lack a Microbial Baseline that can be used as a reference to assess and quantify any changes that we observe. Whilst the incidence of oil spills at sea has over the past 44 years significantly decreased since records began, their frequency in deep waters is predicted to increase as oil exploration operations move further into deeper waters. With respect to the North East Atlantic where the oil industry has operated for over 50 years, our knowledge on the microbiology of this region is severely lacking and has been virtually unexplored. Here we present the development of a Microbial Observatory in the deep waters of the Faroe-Shetland Channel (FSC) where oil exploration is expanding. The focus of this observatory is in understanding how oil-degrading communities would respond in the event of a deep water spill in the FSC, the conditions influencing their behaviour, and a view to developing a site-specific and effective bioremediation strategy. This will be coupled with hydrodynamic modelling to integrate small-scale microbial processes with large-scale physical processes relevant to conditions in the FSC, but with implications more broadly for deep water oil spills. The discovery of novel oil-degrading microorganisms from underexploited biotopes in the ocean will also be discussed, including the application of stable-isotope probing techniques in uncovering these types of organisms.

Aerobic Biodegradation Potential of Oil Hydrocarbons in the Water Column and Deepsea Sediments in the Northeastern Gulf of Mexico

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Previous studies have come to contrasting conclusions regarding nutrient limitation of hydrocarbon biodegradation in the Gulf of Mexico, and rate measurements are needed to support oil plume modeling. Thus, this study investigates the rates and controls of biodegradation in seawater and sediments, largely in the deepsea. Sediment and seawater samples were collected on research cruises in the northern Gulf from 2012 to 2014, where the seafloor was impacted by the Deepwater Horizon (DWH) oil spill. Biodegradation was clearly limited by both nitrogen and phosphorus availability in surface waters with significant rates of CO2 production (0.10 mmol $CO2\ l^{-1}\ d^{-1}$) only observed in nutrient amended treatments. In deepsea sediments, nutrient amendments resulted in 6 fold higher degradation rates (0.49 umol $CO2\ g\ sed^{-1}\ d^{-1}$). From the same deepsea sediments, 30 strains of known oil-degrading bacteria (*Rhodococcus* and *Halomonas*) were enriched and isolated with hexadecane, phenanthrene, and Macondo oil as the sole carbon and energy source. Detection of these strains in sequence libraries indicates that they may have contributed to the degradation of oil deposited onto the sediments.

Rhodococcus strain PC20 degraded approximately one-third of total petroleum hydrocarbons amended into cultures within 7 days. This work elucidates the controls of biodegradation and we provide model pure cultures to elucidate the ecophysiology of hydrocarbon degradation.

Anaerobic Hydrocarbon Degradation by Sedimentary Microorganisms from the Northern Gulf of Mexico

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This study investigates the rates, pathways, and microbial communities that catalyze anaerobic hydrocarbon degradation in areas of the Gulf of Mexico seafloor that were impacted by the Deepwater Horizon blowout. Sediment samples were collected on research cruises in the northern Gulf from 2012 to 2014. Enrichment cultures were initiated under nitrate-, iron-, or sulfate-reducing conditions with Macondo oil, hexadecane, or phenanthrene as the sole carbon source. Microbial activity was confirmed by quantification of electron acceptor utilization. Microbial community structure was characterized through next generation sequencing of 16S rRNA gene amplicons. Results indicate that degradation is most rapid under nitrate-reducing conditions, followed by iron- and sulfate-reducing conditions. Under iron-reducing conditions, enrichments grown with hexadecane showed the fastest hydrocarbon mineralization, followed by phenanthrene and crude oil. Sediment from shallower water depths stimulated faster growth of hydrocarbon degraders than sediment from the deeper sites. Members of the Deltaproteobacteria showed a high relative abundance in all enrichment cultures studied. Surprisingly, known sulfate-reducing groups such as Thermodesulfovibrionaceae and Desulfobulbaceae were enriched under iron-reducing conditions. Evidence suggested the potential for syntrophic hydrocarbon degradation under sulfate-reducing conditions.

Why Is Chlorophyll Elevated Near Natural Seeps in the Gulf of Mexico? Evidence for Bottom-Up, and Top-Down Controls on Planktonic Microbes

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The Gulf of Mexico has a large number of deep (>1000 m) natural hydrocarbon seeps, that release up to 1.1×108 L oil year-1, and while their impact on benthic productivity is well documented, less is known about their impact on surface water organisms. Evidence from ocean-color satellites, as well as shipboard flow-through, and in-situ autonomous-profiler-based fluorescence measurements revealed elevated chlorophyll concentration in surface waters near natural hydrocarbon seeps. We found evidence for the upwelling of nutrient-rich water from depth at these seep sites that could potentially facilitate phytoplankton growth (bottom up control). However, shipboard experiments with surface water samples collected in the vicinity of natural seeps indicated a more complex process. While addition of oil and nutrients (N, P, trace metals), independently increased chlorophyll concentrations, biological oxygen demand (BOD), bacterial cell counts, and enzymatic activities involved in oil degradation, lowered predation (top-down control) also synergistically contributed to these rate processes. The nature of interactions between oil-degrading heterotrophic bacteria, phytoplankton, and their micropredators in these assemblages remains unanswered. Current approaches to investigating

the impacts of hydrocarbons on microbial communities tend to focus primarily on the bottom-up controls, and often overlook the top-down controls and complex food-web interactions that influence these processes. We emphasize this knowledge gap, and highlight the need to consider both, top-down and bottom-up controls in assessing the impact of hydrocarbons on planktonic microbial communities.

Hercules 265 Rapid Response: Immediate Ecosystem Impacts of a Rig Natural Gas Blowout Incident

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In late July 2013, the Hercules 265 natural gas platform in the Northern Gulf of Mexico experienced a catastrophic loss of control. Large quantities of natural gas spewed into the environment for ca. 2 days before the well "self-sealed" by bridging-over. ECOGIG (Ecosystem Impacts of Oil and Gas Inputs to the Gulf) and collaborating GoMRI (Gulf of Mexico Research Initiative) consortia mounted a rapid response cruise aboard the R/V Acadiana to characterize the waters around the Hercules 265 rig, beginning just 4 days after the blowout. Though we could not quantify the duration of the release or the total amount of methane discharged, we documented a clear response by the marine ecosystem to the blowout and could estimate the time scale of exposure of the local water column to the released hydrocarbons. The impact included a significant drawdown of dissolved oxygen to hypoxic conditions, the incorporation of methane-derived carbon into the food web, and the (modest) promotion of nitrogen-fixation at depth. This study highlights the need for focused rapid response efforts in combination with repeated sampling in order to resolve the nature and time scale of microbial responses to sudden environmental perturbations.

Spatial Biogeography of Aerobic Methane-Oxidizing Bacteria at Natural Methane Seeps in the Gulf

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Cold methane seeps represent an important source of carbon to the deepwater of the Gulf of Mexico (GoM) and of methane, a potent greenhouse gas, to the atmosphere. Methane is also a large potential energy source that is readily exploited by microorganisms. Measureable rates of aerobic methane oxidation occur at wide variety of sites throughout the GoM. Much less is known about the diversity and distribution of the microorganisms mediating aerobic methane oxidation. Ongoing studies of the diversity of aerobic methanotrophs have revealed high diversity within the community, suggesting lineage-specific variations in methane metabolism, substrate preference, or both. Less is known about the distribution of these groups in relation to seeps and each other. In this study we use group-specific qPCR primers targeting the pmoA gene, which encodes the enzyme central to aerobic methane oxidation, to investigate the spatial distribution of several groups of planktonic methanotrophic bacteria in and out of methane plumes in the natural seep site GC600. We pair methanotroph abundance data with geochemical data and methane oxidation rates to develop a holistic understanding of the environmental conditions that select for specific ecotypes and the conditions under which the highest

rates of methane oxidation occur. High throughput DNA sequencing of bacterial communities in an out of methane plumes and of pmoA at high seepage sites further describes these methane-utilizing communities. This study advances the knowledge of how methanotroph diversity fills the cold methane seep niche, knowledge critical to understanding water column methane oxidation.

Shifts of Microbial Assemblages as Indicators of Metabolic Potential in the Sediments and the Water Column of the Deepwater Horizon Oil Spill in the Gulf of Mexico (GoM)

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The DWH oil spill released millions of barrels of hydrocarbons into the GoM for over three months in 2010. Since microbiota are sensitive indicators of environmental change, we can use their dynamic responses during spills to monitor a shift in metabolic cycling, including nitrogen, iron, sulfate, and methane metabolisms. While shifts to negative redox reactions occur in oxygen minimum zones and within deep sediments, we hypothesize that oil-contamination shifts the thermodynamic ladder toward negative redox reactions in sediment and water column depths that would not normally experience these shifts. We used Predicted Relative Metabolic Turnover (PRMT), to predict the metabolic potential in 14 metagenomes and 200 simulated metagenomes (predicted with PICRUSt) from sediment and water samples collected during and after the spill. We also applied a combination of modeling (Microbial Assemblage Prediction, MAP), and PRMT to forecast metabolic cycling. Using PRMT, the observed metagenomes showed an increased consumption of metabolites associated with denitrification, iron oxidation, and sulfate reduction of contaminated sediments (0-1 cm) collected 3 months after the spill. Using the simulated metagenomes, we predicted an increase in denitrification throughout the spill in contaminated sediments (0-3 cm) and water column samples. We found evidence of changes in iron reduction and sulfur oxidation in the sediments and water column, and a potential decrease in methane consumption in the water column. We also present a MAP model, from 16S rRNA and metadata from 24 contaminated sediments that predicts the relative abundance of 44 class-level taxa from 9 environmental variables, including hydrocarbon and nutrient parameters.

Using Comparative Metagenomics to Analyze Microbial Degradation of Polar Crude Oil Components

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Following an oil spill, indigenous microbial communities are able to degrade a wide range of crude oil derived compounds. However, little is known about the ability of microorganisms to degrade the polar components of crude oil, which are of significant interest because they are more water-soluble and potentially more toxic to marine biota than the non-polar components. This study seeks to address this gap in knowledge by examining the microbial degradation of the polar components of crude oil in seawater mesocosms. Mesocosms were composed of a seawater bacterial-consortia exposed to crude

oil-derived compounds dissolved in sterile seawater with three sets of controls: (1) sterile seawater with oil-derived water-soluble compounds; (2) a seawater bacterial-consortia amended with succinic acid, which was used as a simple carbon source instead of crude oil; and (3) an unamended seawater bacterial-consortia. All incubation sets were supplemented with nutrients and kept in the dark at room temperature for 14 days. Microbial community structure was analyzed for all treatments using targeted sequencing of the 16SrRNA gene. Preliminary results of mesocosms, which were exposed to crude oil-derived compounds, indicated a shift in the bacterial assemblage compared to control samples. Analysis of the function of the microbial community via shotgun metagenomic sequencing of a subset of these samples is still in progress, but will be integrated with chemical data FT-ICR-MS to enable us to identify metabolic processes responsible for the biotransformation of the polar components of crude oil. Together these data will provide a more complete analysis of the weathering and degradation of crude oil-derived polar compounds in the marine environment.

Microbial Degradation of Polar Crude Oil Components - A Metabolomics Approach

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This study aims to couple Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) analysis with emerging metabolomics techniques to characterize the metabolic products of petroleum weathering and biotransformation of crude-oil derived polar compounds.

Natural marine bacteria consortia were exposed to crude oil-derived compounds dissolved in seawater in a lab incubation study. Three sets of controls were used: (1) sterile seawater with oil-derived polar compounds; (2) seawater with bacteria and succinic acid; and (3) seawater alone with bacteria. All incubation sets were supplemented with nutrients and kept in dark at room temperature for 14 days. Organic matter (including crude oil-derived compounds) from all treatments was analyzed using direct infusion FT-ICR-MS. In parallel, organic matter and microbial biomass were analyzed with liquid-chromatography (LC) mass spectrometry to assess compositional changes in extracellular and intracellular metabolites, respectively. Quantitative LC/MS (with triple-quadrupole mass spectrometer) focused on primary metabolites within base carbon metabolism, while semi-quantitative LC/MS (with FT-ICR-MS) provided an assessment of secondary metabolites and weathering products of hydrocarbon degradation. Preliminary results using direct infusion FT-ICR MS suggest that oil-derived lipophilic polar compounds are relatively more resistant to biodegradation than lower molecular weight non-polar hydrocarbons. Combined with the metabolomic data, we hope to enhance our understanding of microbial degradation of different oil components and estimate the potential environmental fates of weathered and unweathered oil compounds.

Do Chemical Dispersants Impede or Hasten Microbial Degradation of Hydrocarbons in Surface Waters?

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Documenting how chemical dispersants affect(s) rates of microbial hydrocarbon degradation remains a critical question in oil spill response management. Previous experiments applying oil or dispersed oil to a natural deepwater microbial community revealed that the presence of Corexit9500 drove evolution of a different microbial community composition compared with oil alone. Further, hydrocarbon oxidation rates were either the same, or decreased, when dispersant was applied, suggesting that Corexit9500 hindered the hydrocarbon biodegradation. Here, we conducted a similar experiment using a community of microbes collected from a natural surface oil slick in the Gulf of Mexico. Repeatedly over a 3 week period, we quantified the response of the microbial activity and community structure, as well as rates of hydrocarbon oxidation, to oil and dispersed oil treatments. Results of this work will help inform a general understanding of how chemical dispersants affect rates of microbial degradation of hydrocarbons in Gulf surface waters, and how microbial responses differ between surface and deep waters.

Measuring *in situ* Microbial Oil Degradation in Gulf of Mexico Deep-water Sediment using Long-term Benthic Lander Enrichment Experiments

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Weathered crude oil sank to the seafloor following the Deepwater Horizon disaster, essentially removing this oil from further physical and photo-chemical degradation processes and leaving microbial degradation processes as the primary mechanisms for removing this hydrocarbon source. We used a novel in situ benthic lander-based long-term enrichment experiment to study microbial crude oil degradation rates in sediment from a natural hydrocarbon seep in the Gulf of Mexico, and to examine the microbial groups potentially involved in hydrocarbon degradation. Compared to a control experiment, sediment amended with a 1:5 ratio of crude oil had elevated rates of sulfate reduction over the course of the 5-month long in situ experiment, accompanied by methane production towards the end of the experiment. Within the Bacteria, sulfate- and sulfur- reducing and fermentative Deltaproteobacteria and Firmicutes groups were enriched in oiled sediments. From these experiments, we can estimate oil degradation rates in situ, although these are likely higher end estimates for a site that is potentially "primed" to degrade hydrocarbons; additional experiments are needed at non-seep locations. This study can inform the potential removal rates of deep water weathered oil from oil spills.

Session 008
Air-Sea Interactions and Oil Spills: Progression from Semi-Empirical to Physics-Based Models

Air-Sea Oil Spill Interactions: In Defense of Semi-Empirical Formulas

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Spill modeling for Response Support is a complex subject. At all levels, models are simplifications and, when used for Decision Support, should provide detailed information tailored to the decision, options and uncertainty. As this session devil's advocates, the authors argue that spill-scale semi-empirical models with error estimates will provide better guidance than physical models that require extensive idealization of the oil and environment for computational tractability if the observational data or model assumptions are larger scale than the key physical processes affecting the spill. This is often the case for real spills.

For example, transport and spread of surface oil is subject to many underlying forces that can at best be modeled by the use of multiple stochastic parameters. The most famous of analytic oil spreading formulas, the Fay formulas, perform poorly when moved from laboratory to field. Present three-dimensional current models typically lack sufficient boundary and initial data to provide the fine scale resolution necessary for accurate subsurface oil transport estimates. Semi-empirical models are likely to remain the practical option for the near future. The authors will suggest some routes to include more modern and cutting edge processes where sufficient empirical data is likely to be available.

Oily Marine Aerosol Production by Raindrop Splashing

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In this study, we focus on the processes occurring and resulting characteristics of airborne oil droplets generated when large raindrops falling near terminal speed impinge on crude oil layers of varying thickness on the seawater surface. We also investigate effects of premixing the oil with dispersant (Corexit 9500A) and bursting of entrained air bubbles on processes and droplet distributions. High speed imaging and holographic microscopy are used to determine the aerosol formation mechanisms and measure the resulting droplet size distributions. Thousands of microdroplets (< 25 μm) are initially produced less than 0.3 ms after impact. Droplets subsequently ejected from the splash crown rim within 1 to 4 ms post-impact show a bimodal size distribution, with peaks at 50 and 225 μm. The presence of oil increases the droplet production rate from ligaments extending vertically from the crown, as do increasing oil layer thickness and adding dispersants. These trends can be explained by changes to the ligament dimensions associated with an increase in capillary number upon introduction of oil and dispersant. Collapse of the crown also generates a bubble canopy, which subsequently bursts. In this case, the presence of oil and dispersants suppresses droplet generation from this process. These findings provide quantitative data on processes and droplets statistics, the latter of which is essential for modeling of aerosolization of oil slicks by rainfall and associated health concern.

Modeling of Crude Oil Evaporation Using a Bottom-Up Approach: Mass Transfer Considerations and Predicting Potential Secondary Organic Aerosol Formation

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Releases of hydrocarbons from oil spills can have large environmental impacts in both the ocean and atmosphere. While evaporation of oil following a spill is mainly modeled as a mass loss mechanism, the resulting production of atmospheric pollutants can also be a major concern, particularly for continental releases, such as wrecks of river barges or coastal refineries near population centers. Following on observations of significant secondary organic aerosol (SOA) production from the Deepwater Horizon (DWH) spill, we modeled oil evaporation with the goal of predicting SOA formation. We used GC×GC-VUV-HRTOFMS to achieve unprecedented characterization of oil composition from the Deepwater Horizon (DWH) oil spill. Roughly 75% of the total mass of the alkane mixture comprising the oil was classified according to degree of branching, number of cyclic rings, aromatic character, and molecular weight. Such detailed and comprehensive characterization of the DWH oil allows for bottom-up estimates of the relationship between oil volatility and composition. We developed an evaporative model, based solely on our composition measurements and thermodynamic properties, rather than common boiling point parameterizations, which is in excellent agreement with published mass evaporation rates and allows prediction of potential SOA production as a function of wind speed and oil composition. Measured oil volatility distributions were different than previously inferred, suggesting accurate SOA prediction requires detailed oil composition measurements. Wind tunnel experiments verify model accuracy and show that the relative mass transfer of individual components depends on slick thickness and evaporation rate.

Effects of Corexit Components on Oil Alkanes in atmospheric Air/Seawater Interfaces: A Molecular Simulation Study

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1.8 million gallons of Corexit dispersants were used both on the surface and underwater as part of the response to the 2010 Deepwater Horizon oil spill. Our previous combined experimental-simulation studies suggest that aerosolization via bursting bubbles and breaking waves at the sea surface can be an important transport mechanism for the ejection of non-volatile oil spill organics into the atmosphere. Here we report molecular dynamics simulations with the purpose of investigating the individual effects of two of the main components of Corexit 9500 (namely the nonionic surfactant Span 80 and the ionic surfactant dioctyl sodium sulfosuccinate, or DOSS), on the aerosolization of intermediate- and semi-volatile organic compounds from oil (namely linear n-alkanes with 15 to 30 carbon atoms). Our simulation results show that Span 80, DOSS and the n-alkanes exhibit deep free energy minima at the air/seawater interface, indicating that these compounds have a strong thermodynamic tendency to adsorb at the surface of bubbles or droplets. When the air/seawater interfaces are coated with Span 80, the oil n-alkanes show significantly deeper free energy minima than when these interfaces are coated with DOSS. These results are in agreement with our experimental observations in a bubble-column setup, where more oil hydrocarbons are ejected from seawater to air via bursting bubbles when Span 80 is applied to the interface, than when DOSS is present at this interface. Other relevant interfacial properties in these systems will be presented and discussed.

Wavenumber Dependence of Surface Roughness over a Variety of Wind Conditions

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The observation of small-scale ocean surface features, such as capillary waves (surface tension being the primary restoring force) and gravity-capillary waves (surface tension and gravity act as restoring forces), is critical to a number of air-sea interaction processes, including gas transfer, momentum flux, and upper-ocean turbulence. Bringer *et al*. [2013] stated that the discrepancy between leading model wave spectra underscores the need for a greater body of small-scale wave measurements. One approach to bridge this gap, as presented here, is to quantify the specific contribution to energy and surface roughness in specific wave regimes. Here we employ an application of the polarimetric slope sensing (PSS) method, a unique mode of observation for field wave measurements that is both sensitive enough to resolve capillary waves and rugged enough to survive the motions of the observation platform. Results from the data revealed that the contribution of gravity-capillary waves to surface roughness far exceeded that of pure capillary waves. In addition, gravity-capillary waves were found to be the most sensitive to changes in wind speed, with pure capillary waves saturating at low wind speeds (~ 3 m/s) and slow wind speed increases (~ 0.02 m/s^2). The slight roughness contribution from capillary waves and significant contribution from gravity-capillary waves offers insight for scientists in the remote sensing field and important information for the generation of new wave models.

Air-Sea Interactions Observed by Synthetic Aperture Radar

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Synthetic Aperture Radar (SAR) sensors image the surface roughness and motions of the ocean. These two parameters are readily linked to the wind stress, spectral wave properties and surface currents on the ocean surface. These three dynamical and kinematic characteristics also influence the movement of hydrocarbon products such as oil spills and control the response of oil on and near the surface in various bio-chemical and bio-physical processes.

One of the great advantages of SAR data is the large spatial coverage highlighting the sub-grid scale processes and at high enough resolution (sub-mesoscale) to monitor the small scale distribution of oil spills. SAR data has been successfully applied to extract wind speed and direction in hurricane and typhoon conditions and determine the associated spectral wave characteristics. Observations of ocean features such as internal wave solitons, Langmuir cells, frontal features and atmospheric rolls are commonly seen in SAR images. Furthermore, new imaging techniques allow the computation of surface currents associated with various forcing mechanisms. All these variables can be used to describe the fate and response of hydrocarbon products on the ocean surface to air-sea interactions.

Surfactant Associated Bacteria in the Near-Surface Layer of the Ocean

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Certain genera of bacteria in the near-surface layer of the ocean are known to degrade hydrocarbons and produce surfactants, resulting in slicks on the sea surface. Slicks can be observed with airborne or satellite-based synthetic aperture radar (SAR). Here, we report results, which point to a connection between the presence of surfactant-producing bacteria in the upper layer of the ocean and slicks, observed visually and in SAR imagery of the sea surface. Sea slicks formed by surfactants may thus serve as an indicator to the presence of biogenic materials including oil in the water column below the surface, where natural or artificial biogenic material degradation by bacterial communities can take place. In this study, new microlayer sampling techniques developed to address known sources of contamination were used to collect microbial life. We compare samples collected in the Straits of Florida and the Gulf of Mexico. In some cases, sample collection coincided with RADARSAT 2 and TerraSAR-X satellite overpasses. Microlayer and subsurface samples in both slick and non-slick areas were taken for comparisons. Samples were analyzed using qPCR to determine differences in bacterial diversity and abundance in the microlayer and water column. Linking surfactant and oil associated bacteria with SAR may help to identify potential oil spills, which are dissolved in the water column, within a certain range of wind speed conditions.

Observations of Internal Bores Linked to a River Plume in Northern Gulf of Mexico

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Observations of internal wave-like disturbances connected to a supercritical river plume were detected in a coastal region in northern Gulf of Mexico. Satellite imagery revealed a packet of internal waves propagating along the coast of Florida in December 2013. The internal waves were assumed to be linked to a river plume over 14 km away from Destin inlet. Two weeks later, in-situ observations captured a river plume propagating as a coastal current during elevated river discharge, spring tides (~ 0.5 m) and weak wind (< 2.5 m/s) conditions. An Acoustic Doppler Current Profiler (ADCP), a Conductivity Temperature Depth (CTD) profiler, a Vertical Microstructure Profiler (VMP) and two Acoustic Doppler Velocimeters (ADVs) provided current velocities, density and turbulent kinetic energy (TKE) dissipation measurements. Upstream disturbances were identified ahead of the plume through surface roughness features. Bore-like pulses of westward flow transported cold, less-dense plume water in wave-shaped bulges. The turbulent bores contained TKE dissipation values 1.5 times larger than ambient values. Hydraulic theory suggested the bores were phase locked with the river plume, which provided a transport mechanism over long distances, even in a well-mixed regime. Internal waves are typically radiated away from macrotidal river plumes into stratified water. However, these observations show bores locked to a microtidal plume propagating into remnant plume water or well-mixed ambient water and are the first of their kind in this area. The turbulent bores present a mechanism capable of mixing nutrient, pollutant, and/or suspended sediment rich plume water with the ambient coastal environment vast distances away from the plume source.

Physics-based Simulations of Wave-Ocean-Wind Interaction Processes Related to Oil Spill Transport

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The transport and fate of oil spills are largely dependent on the complex interaction processes among turbulent wind, ocean waves, and current and turbulence in upper oceans. In this talk, I will present a suite of physics-based simulation methods developed together with my coworkers in recent years for the tackling of different aspects of air-sea interaction processes at relatively small scales. For moderate wind speeds and non-breaking waves, we have developed a large-eddy simulation (LES) capabilities for turbulent wind and upper-ocean flows on moving, curved grid that dynamically fits the motion of wave surfaces. The surface waves are simulated in a wave-phase-resolved context for realistic, irregular wave fields with broadband spectra. In the wave simulation, nonlinear wave-wave interaction are directly captured, and wind forcing is provided by the dynamic, two-way coupling between wind LES and wave simulation. For high winds and breaking waves, we have developed an LES capability for air and water flows using a coupled level-set and volume-of-fluid method. Our simulation methods have been validated through extensive comparison with measurement data and other simulations. From the high-fidelity, high-resolution simulations using the above simulation tools, we have learned substantial new knowledge on the mechanisms of wind, ocean, and wave interactions, which may be helpful for improving the understanding of and the modeling and capability for oil spills.

Influence of Surface Waves on Ocean Transport and Material Dispersion in Hurricane Isaac and Winter Storms

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Surface wind, waves and currents govern the transport of material on the ocean surface at all time scales. It is a challenging and, yet unresolved air-sea coupled problem, especially in hurricane and winter storm conditions where atmosphere, waves and ocean currents interact in a complex manner. Current ocean circulation models lack not only the dynamics due to sub-grid scale processes, but also the motion induced by wind-generated surface gravity waves, the Stokes drift. In this study, we use the fully coupled, high resolution atmosphere-wave-ocean model, and the surface velocity data obtained during the Grand LAgrangian Deployment (GLAD), to quantify the contribution of waves to total surface velocities and transport during Hurricane Isaac (2012) passage. We find that the hurricane-induced waves advect the surface material in anticyclonic trajectories on the right-hand side of the storm track, and cyclonic on the left-hand side, thus creating an along-track shear in surface velocities. In high wind speeds, the Stokes drift contributes up to 40% of the total velocity and significantly improves agreement with GLAD measurements. In the cases where the initial Eulerian current is in good agreement with observations, adding the Stokes drift significantly improves the prediction of the drifter trajectory. The importance of explicitly resolved waves in a coupled atmosphere-ocean modeling system for oil spill fate prediction is emphasized. The results will be compared with observations and coupled modeling of winter storms during SCOPE in December 2013.

Laboratory Observations of Spray Generation over Fresh, Salt and Oiled Water in Very High Winds

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To determine the effect that sea spray has on the bulk momentum transfer coefficient between the air and water in very high winds a series of comprehensive laboratory experiments were conducted in the Air-Sea Interaction Saltwater Facility (ASIST) at the University of Miami. The spray concentrations due to wind-wave interactions were measured in both fresh and saltwater in very high winds for sizes ranging from 5x10-3 μm to ~600 μm. The results show different size distributions in salt and fresh -water as expected. There was a distinct shift to larger spray droplets in salt water, this is in contrast to the much smaller bubble size distributions and larger overall concentrations of bubbles. Imaging of the air-sea interface during spray generation has revealed the intermittent presences of Kelvin-Helmholtz like instabilities, which may provide a mechanism for the enhanced spume generation.

Session 009
Fate of Oil Droplets – Breakup, Transport, Aggregation and Degradation of Oil Droplets via Physical, Chemical and Biological Processes

Turbulent Crude Oil Jets in Crossflow

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In this experimental study, visualizations follow the evolution of crude oil turbulent jets subjected to a crossflow. Experiments are performed for varying jet speeds, crossflow-to-exit speed velocity ratios, jet Reynolds numbers, premixed Corexit 9500A at various dispersant to oil (DOR) ratios, as well as with and without gas injection. To mimic the cross flow, the oil jets are injected vertically into a 0.9 m x 0.9 m x 2.5 m towing tank containing artificial seawater. High speed imaging follows the evolution and behavior of the jets, both stationary and towed at various speeds. Several means are used for characterizing the droplet size and spatial distributions. For example, a miniature submerged videoscope with pulsed local illumination in the visible and UV range records images of the droplets. Data analysis provides the size and spatial distributions of droplets in the micron to millimeter range. Dynamic light scattering is used to examine the concentrations of micron and sub-micron scale droplets. Results clearly show that bubbles and high DOR modify the plume structure. For high DOR and crossflow speeds, fine oil droplets are trapped in secondary flow structures behind the plume, leading to distribution of oil over a greater depth. These findings provide physical insight into the indirect relationship between dispersant application and plume behavior in crossflow, which can be incorporated into future plume models.

Acoustic Scattering Measurements of Subsurface Chemical Dispersant Efficacy in the Presence of Gas

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To help minimize the effects of oil spills on marine environments, chemical dispersants are applied to enhance dispersion of oil into the water column allowing the oil to be consumed by naturally occurring microbes. Dispersants decrease the surface tension at the oil-water interface causing the oil to break into small droplets. It is generally believed that oil droplets smaller than ~70 microns remain in the water column due to natural turbulence. During the Deepwater Horizon oil spill, 1.1 million gallons of dispersant were injected directly into the blowout of oil and gas at a depth of over 1500 meters. However, there was no way to measure the efficacy of the dispersant at that time. Currently the efficacy of dispersants is determined by measuring the droplet size using a Laser In-Situ Scattering Transmissometer (LISST). LISST instruments are limited to dilute mixtures, below ~500 ppm, because the signal saturates for concentrated mixtures and their windows become occluded by oil. Also, when gas is present the LISST cannot measure the effectiveness of dispersants because it cannot distinguish between the oil droplets and gas bubbles. We developed acoustic measurements which overcome these problems. We quantitatively measured gas bubble size distributions, the mean oil droplet size for surface oil releases, and the percentage of dispersed oil for subsurface releases using acoustic frequencies between 5 kHz and 6 MHz. We performed measurements on four different crude oils (Dorado, Endicott, Troll and OB) for various dispersant-to-oil-ratios (DOR) of Corexit 9500 and various amounts of air in our lab, at SINTEF and multiple times at Ohmsett, where we also tested with methane. Our data show a direct correlation between the amplitude and the frequency response of the acoustic attenuation and backscattering, with the percentage of oil droplets that have a diameter less than ~70 microns and are thus likely to remain in the water column. The acoustic data also showed evidence of interactions of the gas bubbles and oil droplets possibly indicating aggregation. *This study was funded by the Bureau of Safety and Environmental Enforcement (BSEE), U.S. Department of the Interior, Washington, D.C., under Contract Number E12PC00048.*

Partial Dissolution of Oil Drops in a Turbulent Field

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Soluble constituents of crude oil, particularly polycyclic aromatic hydrocarbons, can contribute substantially to the toxicity of the marine environment to aquatic organisms. In this work we study the dissolution of these soluble constituents when oil drops are immersed in the turbulent water column. We adopt an Eulerian-Lagrangian model tracking many thousands of individual oil drops in the turbulent water. The drops are modelled by a standard point-particle model and move under the action of gravity and of the forces applied by the surrounding water, namely drag, lift, added mass, and pressure gradient. The dissolution of the drop soluble constituents is modelled by means of a mass transfer coefficient. The mean concentration of the soluble oil components is studied in its dependence on time, drop population (number, size distribution etc.), and turbulence intensity.

Evolution of Droplet Size Distribution in Deepwater Horizon Blowout: Simulations Using VDROP Model

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Oil droplet size distribution (DSD) plays an important role in the investigations of the fate and transport of spilled oil in the marine environment. This paper used a thoroughly calibrated DSD model, VDROP, which was coupled with an empirical jet model to produce VDROP-J, to evaluate the DSD from the Deepwater Horizon blowout in the near field of the wellhead. The developed VDROP-J model is capable of accounting for the resistance of oil-water interfacial tension and oil viscosity to droplet breakup. Therefore, the model has the ability to predict the DSD in the presence of dispersants. Based on the oil discharge conditions of DWH blowout and local marine environment, different scenarios were evaluated, including with/without the presence of dispersants, varying oil flow rate, gas flow rate and orifice diameters. Comparisons with other models in the simulation of DWH oil spill were also performed. The current VDROP-J model can be easily integrated with fate and transport models to predict droplet behavior over larger scales.

Nanoparticle-coated Oil Droplets Formed Via Bubble Bursting at a Compound Interface

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Bubble bursting at interfaces plays an important role in a spectrum of physical and biological phenomena, from foam evolution to mass transport across various interfaces. For example, due to the wide presence of bubble bursting in nature, such bubble bursting participates in the air-sea interaction by generating aerosol in the atmosphere. Recently, Feng et al. (2014) examined dynamics of bubble bursting in an aqueous phase coated with a thin layer of oil, and documented that this process can disperse submicrometer oil droplets into the aqueous column. These experiments suggest a mechanism whereby the macroscopic oil spill floating at the sea can be drawn into the water in the form of microscopic oil droplets, which assists degradation of oil spills due to the high-surface-to-volume ratio of small particles. Inspired by this observation, we place nanoparticles at the oil-water interface of the system to produce nanoparticle-coated oil droplets by bubble bursting. The application of nanoparticles can lead to more efficient droplet formation and improves the stability of oil droplets. In addition, it also provides the potential to use a force field with appropriate nanoparticles to capture oil droplets. Different parameters are systematically investigated to understand the physical mechanism for better control of the oil droplet formation.

Complex Interfaces, Their Mechanics and Implications

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Dispersant and naturally occurring particles, (including debris, plankton, diatoms and bacteria), alter the size distribution of oil drops in oil spills. While we have some knowledge of surfactant effects for small molecule surfactants, our understanding of particles, and living colloids is less developed. Here, I describe some recent work to understand fundamentally, attachment and interaction of inert particles at fluid interfaces, including trapping energies, pair interactions, interactions of particles with interface shape, and implications for drop interface mechanics. I also describe the formation of biofilms from bacteria-living colloids- at fluid interfaces and their mechanical consequences. I conclude with a discussion of open issues for further inquiry.

Formation of Oil-in-Seawater Emulsions with Nanoparticle and Surfactant Dispersants

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The combination of surfactants and silica or clay nanoparticles and microparticles is shown to provide synergy in the formation and stabilization of oil droplets in seawater. The surfactants lower the oil/water interfacial tension to aid the formation of oil/water emulsions composed of small oil drops (<100 micron diameter), while the adsorption of nanoparticles at the oil/water interface enhances emulsion stability by providing a large barrier to droplet coalescence. The use of particles may therefore reduce the concentration of surfactants required for the dispersion of oil in seawater. To investigate the mechanism of droplet formation, a flowing oleophilic stream containing amphiphiles was mixed with flowing dodecane and then atomized through a nozzle as a function of dispersant type, concentration, and jet velocity. The generation of droplets via jet breakup is interpreted in terms of energy dissipation, Ohnesorge number, Weber number, and Reynolds number. A better understanding of how low concentrations of dispersants (with relatively high oil/water interfacial tensions) may be used in jets to form small oil droplets is of interest for advancing environmental protection in the undesired event of a deep sea oil leak.

Presence of Gelatinous Zooplankton May Enhance Rate of Hydrocarbon Breakdown

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Many studies have examined how oil spills can affect animals, but few studies consider how animals may affect the fate the oil. Gelatinous zooplankton are a ubiquitous group in the Gulf of Mexico and can form dense aggregations in coastal regions. Even during non-bloom conditions, gelatinous zooplankton may process significant portions of the water column. Given that many coastal gelatinous zooplankton species are highly resistant to crude oil exposure, the potential exists for sustained interaction with oil in the water column. Gelatinous zooplankton also release mucus as a means of excretion, defense and in response to stress. Free-swimming medusae produce greater volumes of mucus than corals. Jellyfish

mucus, rich in nitrogen and phosphorus, is known to boost local bacterial populations. Laboratory experiments were conducted to test the hypothesis that the presence of mucus from the common moon jellyfish (*Aurelia aurita*) can enhance the breakdown of crude oil. Seawater, hydrocarbon degrading bacteria, and crude oil were incubated with or without jellyfish mucus for 0, 8 and 14 days. Enumeration of bacteria revealed a significant increase in cell densities in treatments containing mucus after 8 and 14 days. Quantification of alkanes showed a significant decrease in total alkanes for treatments containing mucus. These results suggest that gelatinous zooplankton may play a role in enhancing the breakdown of hydrocarbons after an oil spill.

Probing Interactions of *Alcanivorax borkumensis* with Single Oil Droplets

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Naturally occurring bacteria capable of utilizing hydrocarbon molecules as an energy source inhabit the marine environment, taking advantage of natural oil seeps and exploding in population around oil spill sites. Many of the reported genera of oil-eating bacteria synthesize biosurfactant molecules, which act extracellularly to aid bacterial cells in accessing and utilizing hydrocarbon molecules. *Alcanivorax borkumensis* is a bacterium that dominates bacterial communities around many oil spill regions, and synthesizes a glycoprotein biosurfactant that aids in oil metabolism. Here, we report interactions of *Alcanivorax borkumensis* and its biosurfactant with single hexadecane droplets. Significant interfacial tension changes are measured after the exponential phase of the bacterial growth. *Alcanivorax borkumensis* and its biosurfactant are able to reduce the interfacial tension between aqueous solution and hexadecane. We explain experimental findings using a diffuse-kinetic model. It suggests that the bacterium produces enough biosurfactant to adsorb onto bacterial cell membranes as well as reside in solution. Biosurfactant-induced, agglomerated cells and extracellular biosurfactant both individually lead to a reduction of interfacial tension. When biosurfactant is removed from bacterial cell membranes, hydrophobicity is starkly reduced and cells have little interfacial activity. This suggests that adsorption of biosurfactant onto the cell is vital for bacterial ability to adhere to oil/water interfaces. These findings offer insight into how *Alcanivorax borkumensis* may come to dominate bacterial communities in oil spill regions.

Effect of Motility on Bacterial Encounter Rate with Oil Droplet

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Marine microbes are widely speculated as sources for biodegradation of crude oil. Biodegradation of oil droplets in water column must be initiated by microbes encountering these rising droplets. To measure encounter rate and elucidate key processes, we have developed several microfluidic devices with functionalized substrates by applying layer-by-layer deposition technique to produce a horizontal micro droplet in micro-channels, which provides optical access to observe microbe's movement very close to the oil-water interface. Bacteria and particles are tracked simultaneously over time with high speed microscopy to obtain Langrangian particle kinematics. The encounter events are identified as the trajectory approaches the interface within the distance of one particle diameter. The encounter rate is determined by the ratio of encountering events to particle influx. The high probability encounter sites over the entire oil droplet surface are determined and quantified. To elucidate the importance of active

particle from passive colloids, passive particle, motile and non-motile bacteria are used in the experiments. Additionally, the effects of droplet size, droplet rising velocity, and particle motilities statistics such as angular and linear dispersion, swimming velocity, as well as interface properties such as interface shear and interface curvatures are also assessed in details.

Bacterial Response to Interfacial Stress in a Model of Hydrocarbon Bioremediation

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Microorganisms contribute in alleviating the persistent ecological impacts of oil spills by degrading hydrocarbons. During hydrocarbon bioremediation, bacteria species adopt distinctive community behaviors through cell-cell interactions to compete for nutrients and colonize oil particles. While it is well recognized that such interactions occur in marine environments dominated by interfacial tensions between oil and water, very little is known on the effects of these forces on single cell and the metabolic performance of the oil degraders. We hypothesize that the interfacial tension provokes bacterial stress responses inducing the formation of appropriate protective films, which consequently impede or promote biodegradation. In this study, the response of film-forming cells to interfacial tension was characterized under confinement of Pseudomonas aeruginosa at the interface of hexadecane and water. The interfacial stress generated by such confinements affected the metabolic activity of the cells, as well as the architecture and the mechanics of the interfacial bacterial films. The dynamics between *Alcanivorax borkumensis* cells exhibiting hydrocarbonoclastic properties and P. aeruginosa, whose biofilm stabilized crude oil droplets, were further investigated to comprehend how the interfacial forces impacted biodegradation. Our results demonstrate that preliminary coating of crude oil with P. aeruginosa films reduced surface tension at oil-water interface, which potentially lessen the stress imposed by the interfaces to oil degraders. The understanding of cell response to interfacial stress is relevant to optimize the performance of the bacteria in the oil field, and thereby ameliorate ecosystem recovery.

Session 010
Fate and Transport of Submerged Oil Mats and Surface Residual Oil Balls in Beaches and Coastal Wetlands

Physical Dynamics of Sand and Oil Agglomerates: Field and Laboratory Studies of Artificial Proxies

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Few studies have been conducted on the physical dynamics of sand and oil agglomerates (SOAs, aka surface residual balls) that accumulated offshore of beaches and shoreline habitats after the Deepwater Horizon (DWH) oil spill. These SOAs differ from floating tarballs by their high sand content (80-90%) and negative buoyancy (2107+/-161 kg/m3). In the current study, physically and chemically stable artificial sand and oil agglomerates (aSOAs) were created and tested in the field and laboratory to simulate SOA mobility and seafloor interaction in the nearshore. Lab tests included both hard and moveable (sand) surfaces with oscillatory flows simulating waves, while field experiments in the western Gulf of Mexico

included deployments under shoaling and breaking waves, and in the swash zone. Several existing algorithms for predicting aSOA mobility were evaluated against the lab and field data. A modified Shields parameter that accounted for protrusion of the aSOAs above the seafloor gave the best prediction of mobility, defined as observed incipient motion. Burial, exhumation, and sand ripple formation were observed to influence aSOA dynamics. These results were compared with findings from a numerical model study of SOA behavior following the DWH spill that did not include direct observations of SOAs. Results from these tests can be used to develop a more comprehensive model of SOA dynamics that includes formation, settling, mobility, and breakup.

Bottom Currents and Temperature on DWH Surface Residual Ball Degradation

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Crude oil released by the Deepwater Horizon well blowout picked up seawater and particles while drifting towards the shore. This increased the density and caused the material to settle to the seafloor and form surface residual balls (SRBs) on the bottom. To investigate the degradation potential of SRBs deposited on Gulf of Mexico inner shelf sediments, laboratory incubations were performed measuring oxygen, dissolved carbon (organic and inorganic) and total nitrogen for SRBs of different sizes exposed to temperatures and mechanical stress as caused by water currents moving SRBs along the seafloor. Oxygen consumption rates of different sized SRBs scaled linearly with mass (r^2=0.96, 0.78). Likewise DIC, DOC, and TN production rates increase linearly with SRB mass (r^2=0.56, 0.82, 0.67, respectively), reflecting decomposition. Comparison with sterilized incubations revealed that DIC production and at least 80% of the oxygen consumption and DOC production can be attributed to microbial activity. In contrast, TN values increased at a greater rate in the sterile incubation, suggesting that 27% of the nitrogen released from the SRBs is assimilated by microbes. The rolling of SRBs, similar to that observed in the shallow sublittoral, caused disintegration of the SRBs into smaller oil particles, suggesting wave action accelerates SRB degradation by increasing its surface area and thereby microbial colonization. Incubations of SRBs in a temperature gradient spanning 0°C to 39.6°C revealed a linear increase in oxygen consumption between 7°C and 32°C (r^2=0.92) and no change in rate above 32°C. These results show that environmental conditions typical for the inner shelf of the Gulf of Mexico were conducive for rapid microbial SRB degradation.

Impact of Storm-driven Washover Events on MC252 Crude Oil Fate on Coastal Headland Beaches

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MC252 crude oil on coastal headland beaches and barrier islands are remobilized and redistributed by storm-driven washover events from the beach subtidal and intertidal zones to the beach supratidal and marsh zones. A survey of 59 washover channels across 3 miles of Fourchon Beach, Louisiana found measurable oil in ~10% of the channels indicating the importance of this previously hypothesized transport process across the beach surface. Weathering ratios of alkylated phenanthrenes and dibenzothiophenes in submerged oil mat (SOM) and surface residue balls (SRBs) mobilized during washover events from subtidal areas showed minimal weathering of these compounds relative to poorly degradable C30-hopanes or alkylated chrysenes. As a result, washover events appear to mobilize oil

similar in PAH characteristics to the original oil that reached the shoreline in 2010. SRBs from washovers trapped on the supratidal surface demonstrated significant weathering once deposited (10-90% removal). This weathering occurs over the time frame of months to a year, presumably due to biodegradation driven by enhanced oxygen status on the beach surface. Weathering ratios of PAHs in these tidally-flooded, anoxic washover channels indicated reduced weathering processes relative to supratidal zones but more than subtidal SOM samples. Microcosm studies confirmed the absence of any measurable change in alkylated PAHs under anaerobic conditions. Taken together results suggest that washover events that rapidly move oil into the mudflats and marsh areas contribute to oil persistence when compared with oil forms that are retained on the beach surface.

Long-Term Monitoring Data to Describe the Fate of Polycyclic Aromatic Hydrocarbons in Deepwater Horizon Oil Submerged off Alabama's Beaches

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The 2010 Deepwater Horizon (DWH) catastrophe had considerable impact on the ~ 50 km long sandy beach system located along the Alabama shoreline. We present a comprehensive four-year dataset to characterize the temporal evolution of various polycyclic aromatic hydrocarbons (PAHs) and their alkylated homologs in the residual oil buried in the shoreline environment. The field samples analyzed include the first arrival oil collected from Perdido Bay, Alabama, in June 2010, and multiple oil spill samples collected until August 2014. Our field observations indicate that, as of August 2014, DWH oil is still trapped along Alabama's beaches as submerged oil predominately in the form of surface residual oil balls (SRBs). Chemical characterization results indicate that the PAHs originally present in the MC252 source oil weathered rather rapidly when the oil was floating over the open ocean system (the Gulf of Mexico); however, the weathering rates decreased significantly once the oil was buried within the partially-closed SRB environment. Our data also show that evaporation was most likely the primary weathering mechanism for PAH removal when the oil was floating over the ocean, though photo-degradation and other physic-chemical processes could have contributed to additional weathering. Chemical data presented in study indicate that submerged oil containing various PAHs is likely to remain in the system for a long period. It is likely that the organisms living in these beach environments would have an increased risk of long-term exposure to PAHs trapped in these non-recoverable, buried oil spill residues.

Tar Balls on Elmer's Island, Louisiana: Identifying Technology and Geochemical Characterization

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To better understand chemical processes after oil spills, a combination of remote sensing technology and organic geochemistry analysis was applied to locate tar balls in a shallow subsurface beach environment and identify their origins and extent of degradation. A set of tar balls were collected from the surface and subsurface on the shore of Elmer's Island, Louisiana, where oils from the Deepwater Horizon oil spill have been observed. Subsurface tar balls were detected using Ground Penetrating Radar, with their depths varying from 20 to 60 cm. In addition to whole oil GC analysis, bitumen in tar balls was also separated into SARA fractions for GC/MS and carbon isotope analyses. A variety of

biomarker parameters that serve as source, maturity and biodegradation indicators, such as Oleanane, Gammacerane/Hopane, and 20S/(20S+20R) of C29 sterane, have been assessed. By comparison with previously reported data, biomarkers and carbon isotope compositions of SARA fractions suggested most tar balls were related to the Deepwater Horizon oil spill. Subsurface samples, however, exhibited degradation with varying degrees. The identification of the processes responsible for degradation is in progress. The use of remote sensing and geochemical analysis in this study provides an effective way to uncover tar ball residuals in coastal areas, and pinpoint their sources and delineate associated degradation processes. It may aid in technology development in response to future oil spill events.

Biodegradation of Subsurface Oil in a Tidally-influenced Sand Beach: Impact of Hydraulics and Interaction with Pore Water Chemistry

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We evaluated the interaction between oil biodegradation and the concentration and transport of nutrients and oxygen in a hypothetical beach in the Gulf of Mexico subjected to tidal influences. A numerical model BIOMARUN was developed by coupling the multiple-Monod kinetic model BIOB (Geng et al., 2014, Marine Pollution Bulletin) with the two-dimensional (vertical slice) density-dependent variably-saturated groundwater flow model MARUN (Boufadel et al., 1999, J. of Contaminant Hydrology). It was found that different portions of the beach have different limiting compounds. In the upper intertidal zone, where the inland incoming nutrient concentration was large (1.2 mg/L), oil biodegradation occurred deeper in the beach (thus, nutrient were limiting there). In the mid-intertidal zone, the biodegradation was fast at shallow locations, which was because of the decrease of oxygen concentration with time due to consumption (hence oxygen was limiting there). Oxygen concentration in the mid-intertidal zone exhibited two peaks as function of time. One peak was associated with the high tide, when dissolved oxygen laden seawater filled the beach and a second oxygen peak was observed during low tides, and it was due to replenishment of the pore by oxygen from the atmosphere. The effect of the capillary fringe (CF) height was investigated, and it was found that there is an optimal CF for the maximum biodegradation of oil in the beach. Too large a CF would attenuate oxygen replenishment (either from seawater or the atmosphere), while too small a CF would reduce the interaction between microorganisms and oil in the upper intertidal zone.

Biodegradation and Weathering of Alkylated PAHs in Coastal Marsh and Mangrove Systems

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Weathering and biodegradation rates in oil-impacted marsh and mangrove were measured using time-series field grab samples, CO_2 fluxes coupled with measurement of δ13C of evolved CO2, measurements of porewater nutrient and electron acceptor concentrations and controlled laboratory microcosm studies. Significant weathering of MC252 oil in Fourchon Beach and Bay Jimmy sites were observed with loss of lower molecular weight PAHs (naphthalenes, phenanthrenes and dibenzothiophenes). Weathering rates of approximately 5% per year relative to alkylated chrysenes were observed at the Fourchon sites 3 years after initial oiling. Flux chambers in marsh locations trapped CO2 that exhibited

δ13C signatures lower than indigenous organic matter. The lower δ13C signatures observed were similar to the levels expected from MC252 oil and therefore suggest the potential for mineralization of PAHs in MC252 oil in marsh sites at Bay Jimmy and Fourchon Beach. High-resolution nutrient profiles obtained at these locations during the winter and summer indicate the presence of adequate amount of nitrogen and phosphorous in the marsh and mangrove locations to support biodegradation. High levels of sulfate (> 1000 mg/L) were measured and zones of sulfate depletion coincident with oiled soil layers. Biodegradation of alkylated PAHs in laboratory microcosms with contaminated sediments were observed only under aerobic conditions with first order rates of 0.88-18 /year and no losses was observed under anaerobic conditions. Taken together, results indicate that biodegradation of 3-ring alkylated PAHs is occurring, although slowly (~5% per year), and only in the presence of oxygen.

Microbial Community Analysis of Deepwater Horizon Tar Balls

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The catastrophic 2010 Deepwater Horizon (DWH) oil spill in the Gulf of Mexico released an estimated 4 million barrels of crude oil and an undetermined amount of gases into the overlying waters of the northern Gulf of Mexico (GoM). As a result, oil, oily mousse, mats, and tar balls washed ashore in Florida, Alabama, Louisiana, and Mississippi coastal areas. Tar balls are typically highly weathered products resulting from crude oil spills, which are composed primarily of more recalcitrant (i.e., less biodegradable) components of crude oil. Previous studies have suggested that tar balls may harbor pathogenic bacteria; however, to date, there is a paucity of data concerning the microbial community that resides on and within tar ball structures. In this study, tar balls collected from Dauphin Island, Alabama in June 2010, were characterized utilizing culture-dependent and culture-independent microbiological methods to determine the microbial community structure and potential gene functions associated with microbial colonization of DWH tar balls. Metagenomic data derived from tar ball microbial communities, as determined by next generation Illumina sequencing technology, will be presented. Our findings indicated a prevalence of numerous presumptive hydrocarbon-degrading genes and known hydrocarbon-degrading microbial lineages. In addition, putative pathogenic microbial lineages were also detected. The results of our study provide insight into the resident microbial community of tar balls, including their metabolic potential for degrading hydrocarbons and functioning as fomites for microbial pathogens.

Characterization of the Macondo Crude Oil and Environmental Oil Spill Samples by APCI- and APPI-GC/MS

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We utilize Atmospheric Pressure Gas Chromatography (APGC) combined with tandem mass spectrometry for a trace analysis of petroleum biomarkers from the Macondo wellhead crude oil. Hopanes and steranes (biomarkers) resist biodegradation and are widely used for oil source identification, differentiation, and extent of oil weathering/ degradation processes under various environmental conditions. A commercially available APGC ion source achieves Atmospheric Pressure Chemical Ionization (APCI), producing abundant molecular ions for subsequent MS/MS analysis. The APCI-GC/MS-MS results allow us to differentiate oil spill samples from natural seeps and other crude oils

produced in GoM. We also report the first use of an Atmospheric Pressure PhotoIonization (APPI) source that, in contrast to APCI-GC, is not commercially available. It was developed in our laboratory to selectively ionize aromatic hydrocarbons for advanced source identification and weathering trends. Aromatic hydrocarbons (PAHs and alkylated PAHs) and their sulfur- and nitrogen-containing analogues (PASHs and PANHs), although low in abundance in the Macondo crude oil, persist after release into the environment and have the potential to negatively impact native flora and fauna. Ionization of petroleum compounds under atmospheric conditions (APCI and APPI) with subsequent mass spectrometry detection provides a very sensitive and reliable tool for targeted analysis, fingerprinting the oil source, and tracking a fate and transport of oil spill residues. Work supported by the Florida State University Future Fuels Institute, NSF DMR-11-57490, BP/The Gulf of Mexico Research Initiative to the Deep-C Consortium, Waters Corporation, and the State of Florida.

Biodegradation of Macondo Well Oil in Coastal Sediments: Influence of Temperature and Nutrients

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Coastal environments are especially susceptible to pollution by marine oil spills. However, marine microorganisms are able to degrade many of the compounds in crude oil. As aromatic compounds are generally more toxic than aliphatic hydrocarbons, it is important to be able to predict the degradation rates of different petroleum hydrocarbons in various environments. To test the effects of temperature and nutrients on biodegradation rates and microbial abundance, we incubated sediment with and without oil at two temperatures (4°C or 20°C) and nutrient levels. We used comprehensive two-dimensional gas chromatography (GC×GC-FID) to assess the hydrocarbon degradation of various hydrocarbon classes. We found efficient biodegradation of aliphatic as well as aromatic compounds. Furthermore, we assessed the relative degradation of n-alkanes, branched alkanes, isoprenoids, and various polycyclic aromatic hydrocarbons (PAHs) at various temperatures and nutrient levels.

Aryl Hydrocarbon Receptor Activity of GoMRI Hydrocarbon Intercalibration Experiment (HIE) Samples

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The toxicity of petrogenic Polycyclic Aromatic Hydrocarbons (PAHs) from crude oil has not been adequately assessed. PAHs have variable abilities to activate the aryl hydrocarbon (AhR). PAHs that activate the transcriptional function of the AhR exhibit a plethora of toxic effects. This report describes an attempt to find toxicologically active petrogenic PAHs. I have used a recombinant yeast based bioassay that expresses a human AhR signaling system to interrogate fresh oil and weathered crude extract from a “sand patty” (samples 2779 & 2777) supplied by the GoMRI Hydrocarbon Intercalibration Experiment (HIE). One part oil sample was mixed vigorously with nine parts dimethylsulfoxide (DMSO) or medium (aqueous) and then diluted into the bioassay over 1,000- to 10,000,000-fold range of the original sample. The DMSO extract from the fresh oil was about 100 times more potent than the extract from weathered crude, with the former having activity in the low ug/L range. This result suggests that AhR active compounds decline during weathering process. Aqueous extracts from fresh and weathered oil were over 100-fold lower in AhR activity than the DMSO extract of fresh crude. Comparison of

aqueous extracts from fresh and weathered oil using the yeast bioassay produced AhR activity in the low mg/L range. Actual concentrations of crude oil and PAHs in these experiments are unknown and the values presented above are likely overestimates. Future plans are to use this bioassay toward identification of specific bioactive petrogenic PAHs. Identification of the toxic AhR-activating PAHs will lead to improved predictions for public health and environmental risks from fresh and weathered crude oil.

Session 011
Improving Tools for Marine Oil Spill Response: Lessons Learned and Applied

Science in Support of Decisions: Lessons from Deepwater Horizon

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The 2010 Deepwater Horizon oil spill presented a number of new challenges in terms of well control, spill response, and environmental protection. Scientists from government, academia, and industry focused their attention on providing timely solutions to novel problems to aid decision makers in responding to the crisis. The scientific input benefitted from the establishment of new types of interaction, such as the Strategic Sciences Group (SSG), an interdisciplinary team that performed scenario planning on the potential cascades of consequences of the oil spill from the marine environment through to humans and their economy. In retrospect, the spill response could have benefitted from additional structure. For example, there was much good will in the academic community to want to help in the response, but few communications routes for providing guidance on what research issues are high priority for the response community. The time scale for providing input to decision makers did not permit traditional peer review. The confidence in the science delivered and perhaps the quality as well would have benefitted if there had been established a mechanism to obtain actionable peer review. Overall, the culture of the traditional scientific enterprise is not ideally suited to crisis response, hence the motivation for activating specialized structures.

CFD Study of the Internal Hydrodynamics Affecting a Finite Turndown Ratio in an Oil-Water Separation Hydrocyclone

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Separation of oil from water using a hydrocyclone is an essential aspect for cleaning oil spill and produced water. Hydrocyclone is a device that separates oil and water based on a distinction of centrifugal forces due to a density difference between the two phases. Hypothetically, a tangential feed into the hydrocyclone with a higher Reynolds number generates a greater difference in the centrifugal forces between the two phases which thereby should yields a better separation performance. However, the de-oiling hydrocyclones possess a finite turndown ratio, i.e. it provides acceptable separation efficiency only for a certain range of feed Reynolds number. Reasons of the finite turndown ratio in a de-oiling hydrocyclone have been unclear for more than three decades. This research has identified and explained the source of the finite turndown ratio based on hydrodynamic aspects. The Reynolds

averaged Navier-Stokes equation closed with a transport equation for Reynolds stress is solved numerically for obtaining the pressure and velocity fields in a single cone de-oiling hydrocyclone. Separation efficiency of the hydrocyclone is calculated based on a stochastic tracing of the trajectories of dispersed oil droplets in the flow field. The effects of feed Reynolds number and swirl chamber design on the internal hydrodynamics and pattern of reverse flow core are studied. The separation efficiency of de-oiling hydrocyclones is found to be directly related to the length of reverse flow core. The simulation results motivated redesigning the de-oiling hydrocyclone which yields a wider turndown and better overall separation performance.

Active Bioremediation as a Remedial Option for Oiled Beach Sands

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Biodegradation of crude oil components has been demonstrated as a key component of natural recovery in the deep ocean, and along the beach and marsh shoreline. Active bioremediation is not part of the toolbox of shoreline cleanup techniques, despite advances in the use of these techniques at other sites falling under other risk-based corrective action programs. This paper will present a case study of a beach segment on Fourchon Beach, Louisiana. The use of hard structures on the beach to protect marsh and mangrove areas created conditions for migration and burial of oil beneath the beach groundwater table. A natural feature of groundwater on coastal headland beaches in Louisiana is anoxic or anaerobic beach groundwater which contributes to to oil persistence. At this segment, manual removal of buried oil was performed at a large scale but significant residual oil remains buried in the subsurface. Field and laboratory based data will be presented taregting the ultimate use of biostimulation using oxygen addition. In samples from borings at the site, weathering ratios were constructed by comparing 3-ring PAHs (alkylated phenanthrenes and dibenzothiophenes) with poorly biodegradable C30 hopanes and alkylated chrysenes. Field measurements of beach groundwater chemistry have also been performed in water sampled from piezometers at the site. Laboratory measured oxygen uptake rates of clean and oiled sands were conducted to size oxygen requirements of the bioremediation approach. Laboratory treatability studies demonstrate the influence of O2 on the kinetics of PAH and alkane biodegradation. Design and initial implementation of a full-scale deployment of O2-addition using Waterloo emitters at the Fourchon Beach segment will be presented.

Science Partnerships Enabling Rapid Response (SPERR): Designing a Strategy for Improved Scientific Collaboration during Oil Spill Crises

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The DWH disaster required unprecedented engagement with scientists from multiple disciplines across government, academia, and industry. Although this spurred advancement of valuable new scientific knowledge and tools, it also exposed weaknesses in the system of information dissemination and exchange among the scientists from those three sectors. Limited government communication with the broader scientific community complicated the rapid mobilization of scientists to assist with the response, evaluation of impact, and public perceptions of the crisis. Our project directly addresses the challenges that agencies and industry face in creating effective scientific collaboration practices and operating procedures during large-scale oil spills. The project is actively guided by a team of

stakeholders, including Drs. Jane Lubchenco, David Westerholm, Steve Murawski, Marcia McNutt, and Chris Reddy. In this talk, we will present our findings from 70 stakeholder interviews, and highlight key challenges that hinder effective use of the best available science and scientific minds during a response. We will discuss opportunities for action, including tools that were successful during DWH and strategies from other disaster management fields (i.e. cyber-security, public health) that we have adapted for potential application in oil spill response. Attendees will come away with concrete ideas for how to improve inter-agency and intra-agency rapid scientific collaboration, particularly related to engagement of academic scientists. This talk is a conversation-starter. We will seek active feedback on feasibility, impact, and implementation opportunities, as we will be moving into the final phase of the project in March 2015.

Visualization of Blowout Modeling Output Facilitates Model Evaluation and Impact Assessment to the Water-Column

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Accurately generating quantitative data is the final objective of oil model output and analysis. However, it is often difficult to compare the modeling output with punctuate observations. Here we present a realistic visualization rendering technique to trace the evolution of blowouts and optimize evaluation with observations. The proposed method is coupling the open-source software VisIt with the output of the oil application of the Connectivity Modeling System (CMS). The realistic visualized output is then tested against the comprehensive dataset collected during and post the DWH event by various government agencies and BP. We show how a full four-dimensional visualization of oil concentrations is essential to tune model simulations and improve the model accuracy in predicting the rising of oil to the surface together with the water column exposure. The model optimization is achieved by varying the boundary conditions and parameterization of oil droplets and their chemical attributes, as well as the fate processes (i.e., dissolution and biodegradation). Four-dimensional visualization of oil fraction densities are overlapped with simulated trajectories of pelagic fish larvae from known spawning habitats as an example of the effectiveness of the method in quantifying tradeoffs between water column exposure and coastal impacts during first response.

Scaled Experimental Study in order to Use Unmanned Ships for Boom Towing

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We are exploring the use of unmanned ships for oil spill recovery. The research started several years ago, based on continuous experimentation and analysis of results. The main problem is to devise a suitable control system, so the ships were able to autonomously do recovery operations. In principle, we want no human intervention, just to give the position of the oil spill, and then push a start button. Of course, it would be also possible to permit humans on board, or remote operation, subject to a collaboration policy between humans and control system. We are using scaled ships and a scaled boom. We got from experiments data in order to develop a mathematical model and a simulation environment in which investigate operations before being carried out. The research has achieved three main steps: the on-board autonomous control, the parallel formation control, and the special laws one should consider for boom towing. A series of lessons have been learned, in response to real problems that

appeared during experiments, like the tendency to tug-of-war situations. Recently we achieved complete experimental demonstrations of fully automatic spill recovery. In these experiments an automatic planning is done, and then the ships follow the planned trajectory, deploy near the spill, recover the spill, and then tow it to the desired target place. Nowadays we are starting real scale experiments with small zodiacs. The presentation describes the targets and procedures of the research, emphasizes the new control laws that should be applied for coordinated towing, and discusses experimental results together with a series of videos.

Estimating and Testing Oil Properties Data for Spill Weathering Models

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As oil fate and behavior models become more complex with more sophisticated algorithms, the demand for more extensive information on the nature of the spilled product increases. For example, the NOAA weathering model, Automated Data Inquiry for Oil Spills (ADIOS) at first used only original oil density and viscosity to crudely estimate mass loss and property changes to the surface slick. While the model answers were not precise, the necessary oil data was easily acquired during a spill. The current planned version (ADIOS3) of the model incorporates much more specific oil information such as distillation data and chemical structure statistics on the oil or refined product. Unfortunately, oil property data for modeling environmental consequences during a spill is rarely collected before the spill. Typically, minimal data exists, generated as part of refining or shipping operations. This produces a gap between model data requirements and availability. Emergency response models such as ADIOS3 must have procedures to estimate missing required oil parameters from limited data. This paper examines the approximation schemes and data quality evaluations, developed and tested against the existing ADIOS oil database, used to generate and quality assess missing oil properties. Other modelers may find this set of approximation schemes helpful for their work. Research laboratories may find this set useful for determining which oil properties to collect from new oil samples.

Excitation Emission Matrix Fluorescence of Oil Dispersion: Implications for Petroleum Detection during Spills

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Following the Deepwater Horizon (DWH) blowout, a variety of instruments were used to track spilled oil, including fluorometers. The U.S. SMART guidance document recommends fluorometry as the “most technologically advantageous detection method”. Currently the document refers to in-situ fluorometers, with fixed excitation-emission wavebands. However, during DWH, scanning spectrofluorometers capable of producing 3D excitation-emission matrix spectra (EEMs) proved useful. Fluorescence anomalies in surface waters as well as those correlated with dissolved oxygen depressions at a depth of ~1100m provided evidence of two distinct oiled regions. Thus, high-resolution fluorescence arising from aromatic rings is of great potential for oil fingerprinting. Presented here are the results of dispersed oil-in-seawater experiments conducted on 25 oils at 4 dispersant-to-oil ratios (DOR) using Corexit 9500. Samples were prepared using baffled flasks to physically disperse the oil within seawater. Shown will be

the effect of dispersant on oil-specific fluorescence fingerprints, where shifts in intensity and peak wavelengths were observed. Results will be compared to chemistry results of oil components. Given recent advances with in situ sensors, where lower UV detection is possible, these findings help to discern wavelength regions influenced by dispersed oil within seawater, improve interpretation of fluorescence data, and inform decision-making by responders.

Response System Effectiveness in Reducing the Risk Associated with Large Oil Spills in the Gulf of Mexico

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In the past few years tremendous amount of effort has beenplaced on the safety of offshore operations, both in terms of safe operational procedures and spill response systems. The focus of this study is the effectiveness of these newly built spill response systems called stacks. More than 20 different capping stacks have been built and some of these systems have the capacity to handle 100,000 BOPD, 200 MMSCF/day, shut off against 15,000 psi pressure and can be deployed up to 10,000 ft of water depth within 15 days of time frame after incident reporting. A representative exploratory drilling well from the Mississippi Canyon in the Gulf of Mexico is studied for spill quantitative risk assessment (QRA). The representative reservoir properties for this well are selected from the literature and uncertainties in properties are accounted for by fitting lognormal distribution and carrying out Monte Carlo Simulations. P50 and P90 values from Monte Carlo simulation are used to find worst case discharge rates by using a commercially available multiphase flow simulator with black oil compositional model. Blowout frequency is modeled using Fault Tree Analysis technique and sensitivity analysis showed that unexpected pore pressure and delayed response are the main contributors to the blowout.

A Neural Network Approach for the Detection of Oil Spills Applied to SAR Imagery

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Detection and classification of hydrocarbon films, especially oil spills with spaceborne synthetic aperture radar (SAR), is possible because the effect of these discharges on the ocean surface contrasts with the typical wind-borne undulation of ocean surfaces. Given the scope and impact of events like the Deepwater Horizon oil spill, the need for improved, automated and expedient monitoring of hydrocarbon-related marine anomalies has become a pressing and complex issue to address for governments and responders, as well as the offshore industry. Using active microwave remote sensing systems, we present a method for detecting dark spots corresponding with ocean oil slicks. The method develops, trains, and utilizes a feedforward neural network whose inputs include radar-borne variables (normalized radar cross-section, incidence angle, etc.) and ancillary data (wind speed, textural descriptors). Shapefiles produced by a human-analyst served as targets during the training portion of the investigation. Several hundred images acquired during the Deepwater Horizon event, along with relevant ancillary data, were analyzed to determine algorithm effectiveness as well as optimal conditions for oil detection in SAR data. The algorithm outputs shapefiles identifying the dark regions.

Comparative Analysis of the IXTOC and Deepwater Horizon Blowouts Reveal that Marine Oil Snow Sedimentation (MOSSFA) Maybe the Rule, not the Exception

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Defining the processes that govern a Marine Oil Snow Sedimentation and Flocculent Accumulation (MOSSFA) event are fundamental to predicting the spatio-temporal distribution of spilled oil, planning response strategies and developing quantitative oil budgets. During and after the Deepwater Horizon (DWH), a widespread and temporally protracted MOSSFA event occurred that can be, in part, attributed to oil spill response strategies. To date, the IXTOC-1 (SWGoM, MX; 1979-1980) and the DWH (NGoM; 2010) are the two largest sub-surface petroleum blowouts. An IXTOC-to-DWH comparative study provides a unique approach to juxtaposing sedimentological, geochemical and faunal-microbial parameters to evaluate if a MOSSFA event occurred in the past, and to test whether these events are an unexpected consequence or a predictable outcome of oil-spill response to surfacing oil from subsurface blowouts, including surface dispersant application, oil burning, and freshwater discharge (with abundant nutrients and clays). The physical, chemical, biological and visual characteristics of sediment intervals corresponding to IXTOC-1 and DWH are strikingly similar, suggesting that MOSSFA events occurred during both events and that they share common sedimentary depositional and post-depositional processes. Determining the role of response strategies in causing or augmenting MOSSFA events and their impact on long-term exposure and recovery rates will be discussed.

Session 012
Time Series Studies of Chemical Transformations, Fluxes and Tracers Associated with Accidental and Natural Oil and Gas Releases

A Comprehensive Time-Series of Surface Oil during DWH

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A semi-automated routine (TCNNA) was used to quantify areas of floating oil in 169 SAR images collected during 2010. By interpolating between images that portions of the total floating oil area, we compiled a comprehensive time-series for oil discharged after the Deepwater Horizon (DWH) blow-out. The footprint of floating oil and oil emulsion discharged from Macondo Prospect covered average daily area in the NE Gulf of 7,700 km2; over 97% of this cover comprised thin layers (~1 μm). The ensemble composite of all daily footprints covered a total area of 180,000 km2. Assuming that the balance comprised small patches of a single, thicker class (~50 μm), the average volume per day of floating oil

was 15,000 m3 (SD 9,173, max 41,000 m3; 94,000 and 260,000 bbl, respectively). Floating oil slicks were highly variable during the discharge period. Wind-speed had the strongest effect upon the amount of oil detected by SAR. The DWH discharge far exceeded the input from natural seeps across the Gulf and impacted the NE region where relatively less oil seepage occurs.

Radiocarbon Tracing of the Flux of Petrocarbon to the Sea Floor and Coastal Foodweb Associated with the Deepwater Horizon Event

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The DwH accident released 4.6-6.0 x 1011 g C as oil to the GOM. Radiocarbon measurements on surface sediment organic carbon in a 2.4 x 1010 m2 deep-water region surrounding the spill site indicate the deposition of a 1 cm thick fossil-C-rich layer containing 1.6 ± 1.3 x1010 grams of oil-derived C. This quantity represents between 0.6 to 6.3% of the released petrocarbon with a best estimate of 3.0%. These values are lower limit estimates of the fraction of the oil deposited on the seafloor as they focus on a limited deep-water area of the Gulf, include a conservative estimate of thickness of the depositional layer, and use an average background radiocarbon value for sedimentary organic carbon that produces a conservative value. In addition, evidence of petroleum-derived C entering the offshore planktonic foodweb, as well as widespread oiling of coastal areas suggests that hydrocarbons could have entered the near shore foodweb. To test this hypothesis, we measured 14C and ^{13}C in fish & invertebrate tissue and shells collected within a year of the spill at 7 sites across the northern Gulf. There was a strong correlation between 14C and 13C values in invertebrate tissue consistent with the hypothesis. We observed a west-east gradient with the most depleted 14C values found in Terrebonne Bay and increasingly enriched radiocarbon values in organisms collected at sites to the east. Depleted radiocarbon values as low as −10‰ in invertebrate soft tissue from Terrebonne suggest assimilation of fossil carbon (2.8 ± 1.2%). Alternative explanations include chronic hydrocarbon pollution along the western gulf coast or that the organisms ingest carbon derived from 14C depleted organic matter mobilized during the erosion of coastal marshes in southern Louisiana.

Transformation of Oil in Sediments Constrained Using Advanced 14C Analysis

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Oil deposited on beaches and in coastal marshes from the Deepwater Horizon oil spill has transformed chemically through time but is still present. In fact, oil continues to be a major constituent of organic matter in surficial sediments of those systems (>80% in most cases) based on Ramped Pyrolysis-Oxidation (PyrOx) carbon isotope analysis. Transformation of oil in these environments is important because it results in more thermochemically stable compounds which may be (1) more diagenetically stable also and (2) harmful to the ecosystem but not extractable by normal techniques. Here, we extend our research to shelf, slope, and deep marine sediments to compare observations from different environments. The challenges of employing Ramped PyrOx carbon isotope analysis in the deep sea to

observe oil content and stability include likely smaller concentrations of oil in most of these sediments as well as the patchy nature of evidence of oil incorporation on the seafloor after the Deepwater Horizon event. Close to the wellhead, we observe a shift toward low-temperature pyrolysis of sedimentary organic material within several millimeters of the core tops. We associate this with higher reactivity/volatility of the most recently deposited sediment. Isotopically, if this increased reactivity were due to oil incorporated into the sediment, we would expect lower 14C and stable carbon isotope ratios. However, our observations show that this is not the case. An alternative explanation for this is that the increased reactivity near the core tops is due to increased flocculation of organic material from the surface ocean and/or increased preservation of surface flocculation in the presence of decreased infaunal activity.

Variability and Quantification of Oil and Gas Bubble Release from Natural Seeps in the Gulf of Mexico

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Video data shows that the oil:gas ratios and release rates of bubble discharge from natural seeps in the Gulf of Mexico are significantly variable over a time span of minutes to hours. We use a temperature and pressure logger, and an autonomous video time lapse camera (VTLC) that captures a time series of bubble release to understand the episodic variations in oiliness and release rates. For this study, the VTLC was deployed at two different seep sites, MC118 and GC600 (Mega-Plume). GC600 is one of the most prolific oil producing areas in the Gulf of Mexico with chronic oil slicks visible on the sea surface. The bubble stream examined at MC118 does not contain visible oil; however, we see variations in bubble pulsation. At MC118 (depth: 850 m) the camera captured 10 sec of continuous video, every hour for five days. The gassy bubbles are continuously released from ~9 individual tubes at a rapid rate, and ~4 other tubes turn on and off during the deployment time. At Mega-Plume (depth: 1200 m) the camera captured 10 sec of continuous video, every 30 min for 26 days, including a full tidal cycle. The oily and gassy bubbles are released from a hydrate outcropping where ~2 tubes are consistently active, and various tubes come in and out of activity. An interesting phenomenon seen at Mega-Plume is an intense, sudden, and acute activation of a powerful gas bubble stream. At both sites we see thick bacterial mats, and activity of mobile organisms that interact with the bubble streams in some cases.

Tracing Methane Friction Layer Maxima and Plumes from Natural Hydrocarbon Seeps in Deep Waters of the Northern Gulf of Mexico

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Continuous, in situ measurements of methane concentrations and bottom current speed and velocity in the benthic boundary layer at lease block GC600 in the northern Gulf of Mexico reveal that the formation and horizontal advection of methane-rich plumes originating from natural hydrocarbon seeps are a common occurrence within the friction layer (<100 meters off the seafloor) in deep waters of the

northern Gulf. Multi-sensor measurements at < 1m off the seafloor from benthic landers deployed near 1200m depth for periods up to 48 days measured methane concentrations and current speed and direction at 30 and 120 sec intervals, respectively, finding concentrations ranging from near atmospheric saturation (<3 nM) to over 2000 nM depending on seep proximity and lateral transport speed and direction. A newly developed laser methane sensor deployed by the submersible ALVIN, utilized continuous time-series measurements to document methane injection via rising gas bubble dissolution into the surrounding water column from a well known hydrocarbon seep, Megaplume, finding methane concentrations up to 5000 nM within 0.5 m and < 80 nM approximately 100m away from the seep. Progressive vector diagrams calculated from the acoustic Doppler current data explain the horizontal distribution of near-bottom methane maxima observed in shipboard water column profiles collected near known chains of active seeps at GC600. The instrumented approaches we have developed to simultaneously monitor methane sources and physical processes controlling plume development and transport will enable more effective responses to further accidental hydrocarbon releases while providing a better understanding of the impacts of natural seeps.

Assessing Hydrocarbon Flow through Sediments Using Radium Isotopes

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While the 2010 Deepwater Horizon blowout infused Gulf of Mexico ocean waters with a point-source load of hydrocarbons leading to profound socioecological impacts, natural hydrocarbon seeps routinely deliver diffuse loads of carbon and nutrients to ocean waters. However, current methods to constrain flux estimates from natural seeps (often via remote sensing) offer large-scale estimates without characterizing small-scale seepage variability that is important in shaping the benthic and pelagic ecosystem response. Here, we present a novel method coupling in-situ porefluid 224Ra observations with laboratory 224Ra ingrowth experiments from several oil-rich Gulf of Mexico benthic environments. By using a natural, conservative radiotracer with a 3.6 day half-life, maximum possible 224Ra activities (via radioactive decay principles after ~21 days) are compared to observations to generate in-situ porefluid residence times and resulting 1-D flux estimates to overlying waters. Preliminary results from GC-600 sites (oil seeps) and OC-26 sites (naturally non-oily) indicate flux rates on the order of centimeters per year with a high degree of spatial heterogeneity both within sites and among sites (e.g. oil versus methane seeps). This new approach using Ra to quantify exchange rates between the sediment-water interface lends itself to determining material fluxes in any fine-grained advective environment.

Surface Sediments Became More Reducing Following the BP Deepwater Horizon Blowout Event

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Following the Deepwater Horizon blowout event, sediment cores collected in the NE Gulf of Mexico reveal a region wide sedimentation pulse which resulted in changes to sedimentary redox conditions.

The formation and deposition of mucous-rich marine snow associated with fine-grained clay-sized minerals were the likely cause. Microbial respiration of labile carbon in these fine-grained sediments resulted in decreased pore-water oxygen concentrations and a shoaled redoxcline which produced two distinct solid Mn peaks following the event, in the surface ~ 10 mm, and ~ 20-30 mm depth intervals. Associated with the Mn minimum in sediment porewaters, there is a modest (15-30%) enrichment of solid Re concentration consistent with reducing sediments. Coincident with these reducing conditions, the density of benthic foraminifera decreases 80-93% at some stations, demonstrating the important consequences of changing redox conditions on benthic ecosystem habitability. Next generation sequencing reveals a noteworthy and significant relationship between microbial community structure and redox metal data at mm scale resolution. A time series of three stations sampled over four years following the event reveals that sedimentary Re concentrations increased 3-4 times for the first two years, then decreased, suggesting a return towards pre-impact conditions. Determination of redox sensitive metals will continue to constrain the temporal evolution of reducing conditions, and the possible return to pre-event conditions.

Impacts of Cold Seeps on Nutrient Distributions in the Northern Gulf of Mexico

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The Gulf of Mexico is home to many natural hydrocarbon seeps. One of the largest of these is GC600, which is located 1200m deep in the Northern Gulf. We carried out three cruises to the Gulf of Mexico between 2012 and 2014 as part of the ECOGIG (Ecosystem Impacts of Oil and Gas in the Gulf) Consortium, sampling at GC600 and the surrounding region on each cruise. We used CTD rosette systems and flow injection nutrient analysis to sample and measure phosphate, silicate, nitrate, and nitrite concentrations around cold seeps in the Northern Gulf. We consistently found elevated concentrations of phosphate at GC600 relative to other sites, though silicate, nitrate, and nitrite concentrations were similar across sites. Nutrient availability plays a central role in regulating biological productivity in marine ecosystems, and this contrast in nutrient concentrations between a major cold-seep and its environs represents a fundamental change in the biogeochemical environment. High phosphate availability will favor nitrogen fixation as a pathway for nitrogen acquisition, promoting fundamentally different nutrient dynamics in areas affected by seepage. Cold seeps may play a central role in structuring nutrient and production dynamics in offshore ecosystems of the Northern Gulf of Mexico.

Spatial and Temporal Distribution of Water Column Polycyclic Aromatic and other Petroleum Hydrocarbons from the Deepwater Horizon (DWH) Incident

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There was an unprecedented number of water samples collected from Federal waters during the release of oil from the Deepwater Horizon oil spill. Other petroleum hydrocarbon (OPH including total petroleum hydrocarbons and total extractable matter) and polycyclic aromatic hydrocarbon (PAH) concentration data from water samples published on the Gulf Science Data web site in May 2014 (file W-01v02-01.csv available at gulfsciencedata.bp.com) were downloaded and converted into an R data base for analyses. Reported here are the results of the TPH and PAH concentrations of more than 18,000

water samples, collected from May 5, 2010 to July 21, 2012 from over 13,000 stations. These results included samples collected by multiple response agencies, trustees and BP. The samples were collected in all directions from within a few meters of the well to over 800 kilometers from the well. The highest concentrations were collected near the well head or in samples that appeared to contained oil from surface slicks. Only 7 % of the Gulf Science Data have OPH (TPH and TEM) above the detection limit (200 ug/L) and only 22% of the Gulf Science Data have PAH concentrations above the median of the 394 field blanks (0.056 µg/L). The spatial and temporal distribution of hydrocarbons is presented and compared to EPA benchmarks for acute and chronic toxicity. These data will be made available in Rstudio for use by the scientific community and provide a valuable resource for the assessment of hydrocarbon transport fate and impact.

Four Years after the BP Spill: Distinctive Oxidation Trends of Oil Residue in Louisiana Salt Marsh Sediments Revealed by FT-ICR Mass Spectrometry

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Previous studies report rapid microbial degradation of the Macondo well oil (MWO) in Gulf of Mexico marsh sediments after severe contamination resulting from the 2010 BP Spill. However, the increased compositional complexity of weathered oil requires Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) for molecular-level characterization (1). Here, we catalogue compositional changes that occur to oil contamination extracted from saltmarsh sediments collected from Barataria Bay, and compare molecular transformations in the polar compounds that remain environmentally persistent four years post-spill. Polar compounds increase in relative abundance more than 2 folds after 9 months exposure compared to the parent MWO. Initial oxidation of acidic Ox species occurred across a wide range of O/C and H/C ratios. Surprisingly, most aromatic Ox species were not detected after 41 months. Carboxylic acid incorporation into parent MWO hydrocarbons proceeds over 36 months, with an increase in O2 species from 14.07% after 9 months to 24.64% after 36 months, but decreases to 15.17% after 48 months. This decrease indicates different degradation pathways after initial degradation, consistent with inclusion of multiple oxygen functionalities. Comprehensive compositional analysis advances the understanding of the fate and long- term impact of oil released into the environment. Work supported by NSF Division of Materials Research through DMR-11-57490, BP/The Gulf of Mexico Research Initiative to the Deep-C Consortium, and the State of Florida.

1. A.M. McKenna et al., *Environ Sci Technol* 47, 7530 (Jul 2, 2013).

Time Series PAH Concentrations in Shoreline Mollusks and Continental Shelf Sediments of the Florida Panhandle

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Naphthalene, Phenanthrene, Chysene, and their substituted derivatives (C0-C4) were used as indicators of PAH contamination from the BP MC 252 oil spill along the Florida Panhandle. Surf zone sand and surf zone mollusks (Donax spp.) were sampled along the barrier islands. Continental shelf sediments were obtained by Shipek® grabs from Florida Institute of Oceanography vessels. Sediments were collected as

composite samples and extracted using standard techniques. Clam tissue was processed using a modified Mussel Watch protocol. PAHs were quantified by GC/MS-SIM. The clams had higher levels of PAHs relative to ambient sand. Overall, PAH levels decreased continuously in surf sand, Coquina tissues, and continental shelf sediments, reaching limits of detection (2 ng g-1) within two years of the spill. The surf zone mollusks proved to be useful monitors of bioavailable pollutant exposure along these high energy sandy beach shorelines. PAHs in samples from the continental slope in May 2011 were highest near to the failed well site and were reduced in repeat samples taken one year later. PAHs from continental shelf sediments during the spill (June 2010) ranged from 10-165 ng g-1. Subsequent cruises yielded variable and reduced amounts of PAHs across 27 repeated stations on the shelf through June 2012. The data show that PAHs were distributed widely across the shelf, and their subsequent loss to background levels suggests these compounds were of oil spill origin. PAH half-life estimates by regression were 70-122 days for slope and 201 days for shelf stations, and may inform modeling efforts.

Session 013
Dispersants and Their Components: Environmental Fate and Effects on Organisms and Biogeochemical Processes

Assessing Risks of Crude Oil-Dispersant Mixture on Reproduction - A *Caenorhabditis elegans* Model for Mechanism of Response

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As reproductive stages of organisms are generally more sensitive to environmental stressors than other stages, investigation of crude oil-dispersant mixture effects on reproduction is of fundamentally importance. However, researches on reproductive effects of crude oil-dispersant mixture exposure and its mechanism remain insufficient. The nematode *Caenorhabditis elegans* (*C. elegans*) were employed to investigate impacts of crude oil-dispersant mixture exposures on sex cell development, specifically the processes of oogenesis and spermatogenesis. Wild-type *C. elegans* were exposed to different levels of crude oil-dispersant mixtures (20:1, v/v; at 500 ×, 2000 ×, and 5000 × dilutions) and same levels of oil-alone and dispersant-alone treatments as comparisons. Histological results show that the dispersed crude oil significantly increased the number of apoptotic cells in gonad, indicating oogenesis defects. Also notably immature sperms and abnormal spermatids were found in treated worms compared to controls at all exposure levels ($p < 0.05$), which indicates spermatogenesis defects. The poly aromatic hydrocarbon (PAH) compositions were associated with the phenotype; however did not explain all the reproduction defectives observed. Small RNA molecules termed microRNAs (miRNAs) were major regulators of gene expressions in response to crude oil-dispersant mixture exposure. A variety of reproduction related genes and pathways were found to be regulated by miRNAs following exposure, including MAPK signaling pathway, wnt signaling pathway, hedgehog signaling pathway, and oocyte maturation pathway, etc. This study provides mechanism understandings of impacts of crude oil-dispersant mixture on reproduction.

Sub-Lethal Effects of Corexit® 9500 and Oil on the Eastern Oyster (*Crassostrea virginica*) following Acute Exposure

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Given their particle feeding behavior, abundance in coastal zones, and wide distribution, bivalves are at significant risk for exposure to contaminants such as oil and oil dispersant. Eastern oysters (*C. virginica*) were exposed to Corexit® 9500, crude oil (high-energy water accommodated fraction; HEWAF), and a Corexit®/oil mixture (chemically-enhanced water accommodated fraction; CEWAF) to evaluate potential toxic effects on innate immune functions (phagocytosis and respiratory burst), clearance rates, and histopathology. Respiratory burst appeared more sensitive than phagocytosis to the effects of Corexit® alone, and had a significant negative correlation with Corexit® water and tissue concentrations. Phagocytosis appeared more sensitive than respiratory burst to the effects of HEWAF and CEWAF. Oyster clearance rates were more sensitive to CEWAF than Corexit or HEWAF alone. Clearance rates had a significant negative correlation with Corexit® concentration, but not with HEWAF or CEWAF. The abundance of P. marinus was significantly increased in Corexit®-exposed oysters (10 ppm only), though Corexit® did not affect oyster tissue inflammation. Our experiments have shown that subtle, sub-lethal effects on water filtration rates and immune functions occur following acute in vivo exposure to Corexit®, HEWAF, and CEWAF, with different sensitivities. Data from this study can be used for more accurate risk assessment concerning the impact of oil and Corexit® on the health of oysters.

Ecotoxicological Effects of Oil Spill Dispersants on Sensitive Estuarine Species

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Chemical dispersants are useful tools to mitigate oil spills, but the potential risks to sensitive estuarine species and coastal ecosystems should be carefully considered. To improve the decision making process, more information is needed on the effects of oil dispersants on coastal ecosystems. Dispersant (Corexit® 9500 and Finasol® OSR 52) exposure thresholds for survival were determined for various life stages of several key estuarine species that represent different habitats (water column and benthos), feeding types, and trophic levels. These species included fish, crustaceans, molluscs, and polychaetes. Sublethal endpoints measured included embryo hatching success, larval development, shell or skeletal deformities, cellular enzyme responses, and growth effects. Finasol was generally more toxic than Corexit across all taxa tested. For example, the toxicity in adult grass shrimp ranged from a 96h LC50 of 59.2 mg/L for Finasol to a 96h LC50 of 259.5 mg/l for Corexit. Juvenile clams were the most sensitive species in terms of mortality to both dispersants. Other endpoints showed that Finasol and Corexit also decreased hatching success in grass shrimp and sheepshead minnows. Expected outcomes include developing a suite of contaminant-toxicity thresholds, having a basis to help inform management decisions, and the ability to apply to a variety of oil-spill events in which dispersant use may be considered.

The Impacts of Macondo-252 Crude and Corexit-9500 on Embryonic Development in the Gulf killifish, *Fundulus grandis*, Subjected to Varying Salinities

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The chemical profile of crude oil will change over time due to natural weathering, a process that is influenced by environmental factors such as salinity. Natural weathering and the addition of chemical dispersants increase the rate of dissolution of oil into the water column; consequently, they increase the rate of biodegradation, affecting the bioavailability of the toxic components of crude oil to aquatic organisms. Although little is known about the mechanisms of toxicity for many of the chemical components of crude oil, recent studies have demonstrated that different constituents in crude oil will elicit different toxicological effects in aquatic organisms. In the current study, the early life-stage effects of weathered water accommodated fraction of dispersed surrogate Macondo-252 crude oil on Gulf killifish were assessed at concentrations of 12 and 18 g/L seawater. In both salinity treatments, reductions in hatching success and bradycardia were observed in embryos exposed to oil-dispersed treatment waters weathered up to 4 weeks, with toxicity decreasing over time. Embryos incubated in 4 week weathered oil in 12 g/L seawater exhibited decreased hatching success and increased time to hatch, suggesting a time- and salinity-dependent mechanism of toxicity different from oil-dispersed waters. These data demonstrate how environmental conditions can influence the biodegradation of crude oil, and, in turn, affect biological responses.

Effects of Weathered Oil and Dispersants on Hatchling Morphology, Apical and Molecular Endpoints of *Menidia beryllina* Embryo

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Exposure of fish embryos to relatively low concentrations of oil has been implicated in sub-lethal toxicity. However, the effect of oil and dispersants should be more thoroughly evaluated to better understand and anticipate the ecological impacts. Oil (1ppm) and Corexit dispersants (9500 and 9527-0.1ppm) were weathered singly and in combination in 25ppt saltwater for 7 days. The aqueous part post-weathering (WS) was diluted at 200ml WS: 800ml 25ppt saltwater. *Menidia beryllina* embryos at 30-48 hrs post-fertilization were exposed in quadruplicate for 72 hours as follows: Control (1 liter 25ppt Saltwater), weathered Oil (200 ul/L), C9500 (20 ul/L), C9527 (20 ul/L), Oil/9500 (200/20 ul/L) and Oil/9527 (200/20 ul/L). Mortality, heartbeat, embryo normalcy score and abnormality types were recorded. The QPCR assay was used to quantify abundances of transcripts of target genes: Vitellogenin, CYP1A, HSP90, StAR, GhR, CYP19b, IGF-2, AMH, DMRT1 and Choriogenin L; GAPDH served as the housekeeping gene. Mortality was not significantly different between treatments (p=0.68). The lowest heartbeats and normalcy scores respectively were recorded in Corexit 9500 (67.5 beats/min and 60%) and 9527 (67.1 beats/min and 44%) exposed embryos compared with control (82.7 beats/min and 100%). Although oil and dispersants exposed embryos developed to the hatching stage; significantly more embryos were in a state of deterioration, with arrested tissue differentiation compared with controls (p=0.008). Developmental abnormalities were induced in *Menidia* embryos. It is expected that the molecular endpoint would be an early indicator of the long term effects of oil spill and dispersants.

Bioavailability of Oil in Different Laboratory Aquatic Exposure Systems: Passive, Physical, and Chemical Dispersion/Dosing Methods

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Understanding and correctly quantifying risks to aquatic life from petroleum substances such as crude oils and fuels is an important part of Net Environmental Benefit considerations in spill response. The nature of the exposure is considered an important factor in evaluating the risk to aquatic life. How important are oil droplets in the toxic response? Are only soluble hydrocarbons bioavailable? In order to provide a consistent evaluation of the impact of droplet oil we developed three dosing systems in freshly collected seawater and freshwater: passively dosed through silicone tubing, and a mixing system (25% vortex) with and without COREXIT 9500 dispersant. The test substance (Endicott crude oil) and exposure waters were comprehensively characterized using GCxGC, GCMS of extracted oil, and passive samplers. The results confirm the gradient in droplet concentration in the exposure systems: Trace levels (<0.1 mg/L) in the passively dosed system closely matching the theoretical dissolved hydrocarbon profiles, and 0.5 to 5 mg/L in the physically and chemically dispersed preparations. Effects of short-term exposures to *D. magna* and *M. bahia* correlated strongly with predicted dissolved toxic units and with the bioavailable hydrocarbons measured using the passive samplers. We conclude that droplet oil appears to have minor impact in these aqueous exposures at the concentrations studied here (<5 mg/L), suggesting that hazard assessments may discount the presence of droplet oil in dilute systems.

Long Term Persistence of DOSS in GOM Sediments

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DOSS, bis(2-ethylhexyl)sulfosuccinate, is one of the main surfactant components of Corexit 9500 and 9527A. Little data exists describing the spatial distribution of DOSS in GOM sediments between 2010 and 2013, in part due to the need to develop selective and sensitive analytical methods. A method for the exhaustive extraction of DOSS from GOM sediments and for the quantitative analysis of DOSS in these extracts via LC-ESI-MS/MS was developed and applied to sediment cores collected in the GOM between 2010 and 2013. Two stable-isotope labeled internal standards for DOSS and one quantitative transition and two qualitative transitions for DOSS were used to identify and quantify DOSS. Our data suggest that DOSS is persistent in deep-sea sediment cores collected from two sites near the Deepwater Horizon (DWH) well-head more than 3 years after the original application of Corexit in response to the DWH oil spill. Specifically, DOSS was found between 0.5-1 ppb in the top 3 cm of five cores collected from Mississippi Canyon (MC) Federal Lease Block 297 and one core collected at MC294. Sediment DOSS concentrations observed at MC297 for 2012 and 2013 cores are comparable to those from 2010 collected within the same lease block, indicating no discernable decline in the concentration of DOSS under the prevailing sediment conditions in the GOM. Additionally, the large scale spatial distribution of DOSS in GOM sediments for multiple sites within 75 km of the DWH well-head will be discussed.

Characterization of Transformation Kinetics and Products of Corexit® 9500 in Seawater Using High Resolution Mass Spectrometry

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Corexit® 9500 dispersant was extensively applied during the Deepwater Horizon oil spill in 2010 to mitigate the impact of crude oil on sensitive coastal ecosystems; however, the transformation rates, products, and toxicity of Corexit remain largely unknown. Corexit dispersants contain a complex mixture of solvents, anionic and nonionic surfactants including ethoxylated sorbitan, ethoxylated polysorbate esters and dioctyl sulfosuccinate (DOSS). Since biodegradation is a suspected pathway of Corexit transformation, we conducted aerobic, bench-scale shake-flask biodegradation experiments with Corexit in coastal seawater. Samples were collected daily for the first seven days, and biweekly for the remaining 35 days of the experiment and analyzed by TOC analyzer and by high-resolution mass spectrometry (HRMS) for surfactant characterization. Preliminary TOC results revealed limited mineralization of Corexit over the course of the incubation. These results warranted further investigation using HPLC-HRMS and MS/MS to identify the surfactant transformation products and kinetics using high mass accuracy and fragmentation analysis, with concurrent charged aerosol detection (CAD) to quantify individual components and the evolved transformation products. Initial transformation product analysis revealed that while some components (e.g. polysorbate monoesters) are quickly attenuated by transformation, others (e.g. DOSS) are more persistant. Further results to be discussed include comparative biotransformation kinetics and implications of our findings on the eventual fate and disposition of Corexit dispersants in the marine environment.

Intercomparison of LC-MS-based Approaches for Determining the Chemical Composition of Dispersant Formulations

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Detailed characterization of oil spill dispersants can be important for addressing many questions; e.g., molecular modeling of surfactant oil interactions or mapping of transformation pathways. We report here results from complementary LC-MS based approaches for comprehensive characterization of surfactants in Corexit formulations. We have compared those compositions with literature reports for both Tween surfactants and Corexit 9500. Mass spectrometric analysis by time-of-flight MS (6000 resolution) and Orbitrap MS (100,000 resolution) have revealed the identities of nearly 1000 distinct nonionic surfactant structures present in polysorbate (e.g. Tween-series) and sorbitan ester (e.g. Span-series) surfactants. Results are constrained by parallel analysis with a charged aerosol detector. Accurate mass analysis allowed separation of a myriad of ethoxylated series of isobaric polysorbate surfactants (differing by 0.088 amu). Fatty acid ester distribution analysis (and MS-MS) has enabled separation of isosorbide ethoxylate and polyethylene glycol esters with identical formulas, and found to represent the major compound classes in Tween products. High-resolution MS analysis showed that sorbitan esters in Span 80 contain a more complex and hydrophobic mixture of fatty acid esters than previously recognized, with important contributions of di-, and tri -esters. Samples of Corexit 9500 contain polysorbate fatty acids that are much more unsaturated than those found in commercial Tween 80 and 85. We will explain why our instrumental approaches yield different estimates of molecular compositions and highlight the value of complementary analytical approaches for characterizing these complex mixtures.

Session 014
Impacts from the Deepwater Horizon Spill on Deep-Sea Ecosystems: Detection, Causes, and Effects on the Benthos

Persistent Impacts to the Deep Soft-Bottom Benthos One Year after the Deepwater Horizon Event

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In September-October 2010, three to four months after the Deepwater Horizon blowout was capped, a zone of moderate and severe impacts to deep-sea soft-bottom benthos was identified that extended over an area of 148 km^2. The impact was a loss of -53.7% of macrofauna family diversity and 38.3% of meiofauna major taxa diversity in the most severely impacted zone. The area was resampled in May-June 2011, 10-11 months after the event to determine if the identified effects were persisting. The sampling design compared 19 stations in the impact zone to 13 stations in the reference zone that were sampled in both years. While there were some signs of recovery in 2011 (particularly in the meiofauna), there was evidence of persistent, statistically significant impacts to both the macro- and meiobenthos. Macrofaunal richness and diversity in 2011 were still 17.9% and 28.6% less, respectively, in the impact zone than in the surrounding area and meiofaunal richness was 21.9% less in the impact zone than surrounding area. The persistence of significant biodiversity losses nearly one year after the wellhead was capped indicates that full recovery has yet to occur.

Mediating Effect of Phytoplankton-related Marine Snow in Oil Fate and Deep Sea Benthic Ecotoxicity

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Increased production of marine snow was reported during the Deepwater Horizon oil spill. It is believed that this process enhanced sedimentation of oil, particles and surface plankton which could explain the toxic layer on the sea floor that currently still persists and prevents the benthic ecosystem from recovering. In laboratory studies that were conducted within the C-IMAGE research consortium we showed that oil spill dispersants induce the production of extracellular material ('sea-snot') by plankton. Dispersed oil droplets and clay particles are captured within this sea-snot. The latter making the complexes negatively buoyant, resulting to enhanced sedimentation rates. This complex process was found to be much more efficient in transporting oil from the water column to deeper layers than when only clay, or clay and dispersants without sea-snot are present. In these situations dispersant application can thus concentrate the oil in a toxic sediment layer and greatly enhance its persistence in the environment. This mechanism should be taken into account when deciding on oil spill response measures in situations with phytoplankton blooms and suspended particles. We intend to study the consequences of this type of oil sedimentation on the benthic community including chances for recovery. We expect that this will add to our understanding of biological consequences of the Deepwater Horizon oil spill for the benthic ecosystem, and to be better prepared for future spill situations.

Rapid Sedimentation, Resuspension and Redistribution of Hydrocarbons in the Wake of the Macondo Blowout

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A rapid sedimentation pulse to the seafloor was documented across a large area in the Gulf of Mexico following the Macondo Blowing in 2010. This sedimentation event was short lived (~3 months) but it was widespread and transferred a significant amount of material from the ocean surface to the seabed. The sedimentation pulse was fueled by biological processes, microbial production of marine oil snow, but likely exacerbated by the burning of oil on the sea surface and widespread dispersant application. Together, these processes transferred weathered oil, biologically-derived materials, and burn-derived materials to the seafloor in a manner not previously recognized or documented in the environment. The benthic biological impacts of this sedimentation event were widespread and included negative effects on microbial, infaunal, as well as deepwater coral communities. Once on the seafloor, even in deepwater (>1500m), this material is subject to repeated episodes of resuspension following storm events. Resuspension redistributes potentially toxic hydrocarbon residues over likely significant areas with probably long-term and widespread impacts on deepwater and benthic biological communities.

Effects of High Pressure on Hydrocarbon-degrading Bacteria

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The wellhead of the DWH drilling rig is located at a depth of 1,500 m. Here, at a hydrostatic pressure of 150 bar, 4.9 million barrels of oil gushed out into the Gulf of Mexico (GoM). All previous studies investigating the bacterial degradation of the DWH oil were conducted at ambient pressure. We investigated the degradation of mineral oil components at pressures up to 150 bar. With our work we prove that pressure is an important factor that has an influence on the bacterial degradation of hydrocarbons. Using high-pressure lab technology we investigated the impact of high pressure on the biodegradation of oil components by different model strains. *Rhoddococcus qingshengii* TUHH-12 was able to degrade different alkanes at 1 bar as well as at 150 bar at similar rates. In contrast, the aromatics-degrading strain *Rhodococcus wratislaviensis* showed an enhanced growth on toluene at 150 bar compared to growth at atmospheric pressure. The opposite result was observed with *Sphingobium yanoikuyae* B1, a degrader of polycyclic aromatic hydrocarbons. At pressures higher than 120 bar this strain showed no growth with naphthalene at all. Thus, we show that high pressure can have both an enhancing and an inhibiting impact on growth of hydrocarbon degraders. Our results reveal that pressure needs to be considered as a crucial factor that cannot be neglected in investigations of oil biodegradation in deep-sea environments. Further research is in progress investigating the effect of high pressure on oil degradation by bacterial communities and strains from sediments sampled in the GoM.

Analysis of Oil Spill Impacts on Shipwrecks: Implications for Archaeology, Microbial Ecology, and Ecosystem Monitoring

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Shipwrecks serve as artificial reefs in the deep ocean. Due to their random distribution and inherent diversity compared to the surrounding environment, shipwrecks are ideal ecosystems to study pollution impacts and microbial distributions. This study comparatively assessed the Deepwater Horizon spill's impacts on shipwreck microbiomes and the synergistic effects of contaminants on these communities and the structures that support them. Wooden-hulled and steel-hulled shipwreck microbiomes in the northern Gulf of Mexico were investigated. Samples from in situ biofilm monitoring platforms deployed adjacent to shipwrecks and sediments collected 2-200m from each site were evaluated for shifts in microbiome structure and function relative to spill proximity and spill-related contaminants in the local environment. The study's goals are to identify impacts to recruitment and community structure at sites located within and outside of spill-impacted areas. Taxonomic classification of dominant and rare members from shipwreck microbiomes and metabolic information extracted from sequence data yield new understanding of microbial processes associated with site formation. The study identified microbial inhabitants of shipwrecks, their role in site preservation, and impacts of the 2010 spill. This approach could inform about the role of microorganisms in establishment and maintenance of artificial reefs as well as provide information about ecosystem feedbacks resulting from spills.

Sedimentary Evidence of Abrupt Environmental Changes after the Catastrophic IXTOC Oil Spill and/or Chichonal Volcanic Events in the Southern Gulf of Mexico

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Sediment box cores from the southern Gulf of Mexico were analyzed to understand changes that have occurred in the sedimentological regime, geochemical conditions and faunal responses over the last 100 years. This interval spans 2 regionally significant catastrophic events: the IXTOC sub-surface petroleum release in 1979-80 and the eruption of the Chichonal volcano in 1982. Many of the sedimentological, mineralogical, biological and geochemical proxies show an abrupt and significant change at depths between 3 to 8 cm, where sediments are dark brown and are comprised predominantly of lithic components, including volcanic ash. Within this interval, foraminiferal shells were scarce and poorly preserved (broken), contain bituminous infillings/coatings and record a negative shift in their 13C. The decrease in foraminiferal abundance could have been due to dilution by the increase in lithic particles and/or mass mortality related to either catastrophic event. Magnetic susceptibility and elemental concentrations (e.g., Mn, Ti, Ni, Mo, Cr, Fe, Cu and Zn) showed maximum values also suggesting changes in inorganic geochemical inputs and intensification in redox conditions. Most of the measured parameters exhibit a gradual return to baseline, pre-catastrophy, levels from ~1985 to present. In the recent interval, foraminiferal populations indicate that the recovery of the meiobenthos community has occurred in less than 30 years following the catastrophic events.

Quantifying the Ecological and Chemical Impacts of the DWH Event on Benthic Foraminifera and Rates of Subsequent Recovery (2010-2014)

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A time-series of sediment cores collected from the Gulf of Mexico (2010-2014) were used to assess the spatial and temporal impacts on the benthos, quantify the recovery of benthic foraminiferal (BF) community structure and shell chemistry (δ13C) following the Deepwater Horizon (DWH) event. A significant decline in BF density (80-93%) and diversity recognized since 2010 has been attributed to both a 2-3-fold increase in polycyclic aromatic hydrocarbon concentrations and increasing reducing conditions in surface sediments. At certain sites, a recovery in density occurred in late 2011, while at other sites density did not recover until 2012. Independent of location, the δ13C record of BF carbonate showed a marked depletion in 2010 that has further intensified through 2012. This suggests that BF not only incorporated petroleum carbon into their shells directly following the DWH event, but that they were continually respiring a petroleum carbon source for more than two years afterwards. Using a δ13C mass balance approach, 10-20% of total respired carbon assimilated into BF carbonate from 2010 to 2012 was comprised of petroleum carbon. BF community structure change and trophic implications over this time-series will be discussed. This continuing research identifies specific biological responses to physical and chemical changes in the sediments and identifies benthic community recovery rates following a deep-water petroleum release and its accumulation in the sediments.

Initial Findings of Macrofauna Community Structure within the DeSoto Canyon

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Macrofauna, sediment-dwelling invertebrates ≥ 300 µm, whose major representatives include polychaetes, bivalves, and assorted crustaceans, have long served as indicators of benthic ecosystem integrity. The 2010 Deepwater Horizon oil spill remains largely under-characterized for the DeSoto Canyon in terms of deep-sea impact. Using macrofauna to evaluate benthic impacts, we sampled sediments from 12 sites along and across the axis of the canyon, ranging in depth from 479-2310 m, using replicate lowerings of multicorer. We present the initial findings of the deep-sea macrofauna community structure from all 12 stations sampled in 2012, the first of a 3-year sampling scheme, along with two control stations outside the canyon sampled in 2013.Polychaetes compositionally dominate followed by tanaid crustaceans and bivalves. Based on preliminary analyses, the total number of individuals was not correlated with depth. However, the total number of taxa and species richness were significantly correlated with depth. Rarefaction shows XC4 (2310 m) had the lowest diversity and NT800 (800 m) had the highest. Using multivariate statistics, structurally, communities fall into 9 clusters. Overall, community structure differed between canyon sites as compared with non-canyon controls. Environmental data was available for 10 canyon sites and a BEST analysis for these sites demonstrated latitude and turbidity in combination with either depth or salinity to be the strongest correlates with community structure. Further analysis by DISTLM largely supports the BEST results. As we process data

from more stations and time points, we hope to better evaluate the environmental factors that are related to the observed patterns in community structure.

Deepwater Horizon (DWH) Oil Spill: Assessment of Potential Impacts to the Offshore Benthos and Sediment Quality along the Gulf of Mexico Shelf

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Field surveys were conducted along the SE Gulf of Mexico shelf in May 2007 before the DWH spill, the NE shelf in August 2010 one month after the wellhead was capped, and the NW shelf in August 2011 one year later to assess status of ecological condition and potential stressor impacts in these offshore waters with a focus on the soft-bottom benthos and sediment quality. Samples were collected at 134 stations (7 – 100 meters deep) for multiple types of analyses including condition of benthic infauna, sediment toxicity, concentrations of oil and other contaminants in sediments and fish, and basic habitat parameters. A probabilistic sampling design was used to support statistical estimates of the spatial extent of condition with respect to these indicators. Results showed no evidence of obvious changes to the benthos due to the oil spill. All measured contaminants, including oil indicators, were at low background levels below probable-effects sediment quality guidelines and within pre-spill ranges. Multivariate analysis of the benthic data showed strong correlations with other natural and anthropogenic controlling factors such as dissolved oxygen (DO), grain-size, depth, and longitude. Lowest values of benthic species richness were most prevalent at stations closest to the MS River, coinciding with lower DO and muddier sediments and with areas of well-documented seasonal hypoxia. These results provide a record of the status of ecosystem condition in offshore waters of the Gulf, serving as a basis for understanding where and to what extent DWH injuries have occurred as well as a baseline for evaluating future change due to natural or human influences. Future work should include long-term monitoring of these resources as a tool for change detection.

Natural vs. Anthropogenic Oil: An Ecological Comparison

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In the Gulf of Mexico, hydrocarbons are naturally released through seeps in the seafloor at thousands of locations. Hydrocarbons also enter the marine environment derived from human activities including surface runoff and oil spills such as the 2010 Deepwater Horizon (DWH) Blowout. Recent studies have shown that the DWH oil blowout significantly altered macrobenthic communities several kilometers around the wellhead, with communities near the wellhead being significantly more impacted than those further away. A comparison between natural seep and spill-impacted communities has not been performed, despite the potential of both sediment types to contain significant concentrations of hydrocarbons. Macrobenthic community abundance, diversity, and structure were analyzed at sites near and far from hydrocarbon seeps collected in 2012 and 2013 and compared to benthic communities collected at various distances from the DWH wellhead in fall 2010. We tested the following hypotheses: (1) Communities near the wellhead are different from communities near natural oil seeps (2) Hydrocarbons affect animals differently dependent on the constituents of the oil (3) Animals associated with natural seeps are more likely to survive and persist in areas contaminated by DWH oil compared to

non-seep associated infauna. Characterizing natural seep communities is important for understanding macrofaunal community dynamics in the presence of hydrocarbons and provides baseline data for future restoration activities.

Post-Spill Response of Cold-Water Coral Associated Benthos in the Gulf of Mexico after the Deepwater Horizon Oil Spill

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Oil-spill impacts to benthic communities have been documented in multiple deep-sea habitats, including soft sediments, cold-water corals, and coral-associated benthos, as a result of the Deepwater Horizon event. However, the long-term response to oil exposure and the length of recovery time for these communities is still unclear. Here we examined deep-sea coral-associated benthic macrofauna at a single impacted site to assess for post-spill changes in the sediment communities. Sediment cores were collected annually from 2010-2014, near deep water octocorals in Bureau of Ocean Energy Management lease block MC294 after the spill occurred. Sediments were analyzed for macrofaunal density, diversity, community composition, sediment grain size and organic content. Benthic community structure differed among years; polychaetes dominated the communities early on, while contributions of molluscs and crustaceans increased over time. Oil residue was present in upper sediments for multiple years post spill, suggesting a slow turnover of oil within sediments. Although pre-spill data are lacking for most deep-sea coral habitats, these multi-year data provide a baseline for assessing the recovery of benthic communities in future monitoring and restoration activities.

Mechanisms of Impact from the Deepwater Horizon Oil Spill to Corals and Associated Communities in the Deep Gulf of Mexico

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The DWH oil and gas release was unlike any previous major hydrocarbon spills because of the direct release of hot oil and gas at 1400 m depth into cold benthic seawater and because of it's long duration and resultant extended use of dispersant and other methods to both limit production of surface slicks and sink/disperse the oil that arrived at the sea surface. As a result this spill had the potential to adversely affect deep-sea communities through two distinct mechanisms. The release at depth resulted in a plume of oil/gas and potentially dispersant that remained at depth and traveled over extended distances with the potential to damage organisms and communities in its path. Secondly, the extended presence of surface slicks over large areas, and extensive burning and aerial application of dispersant contributed to the production of sinking particles that may also have been toxic to benthic organisms and communities below the slicks. In this session several papers will examine the effects of the spill on benthic organisms in the deep sea while others will report on laboratory studies of the effects of oil, dispersant and mixtures of the two on deep-sea organisms. At some of the impacted sites that will be discussed today, their locations make it much more likely that the effects observed are due to one or the other of the mechanisms suggested above. At other sites it is less clear which mechanism was responsible for the effects observed, but the direct evidence pointing to a particulate, or at least not evenly dispersed impacting agent for the corals and will be presented.

Oxygenation in Deep-water Coral Communities of the Northern Gulf of Mexico

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Acute impacts from the blowout of the Macondo wellhead in 2010 have been documented for several deep-water coral (DWC) communities in the Northern Gulf of Mexico. Photomosaic images and video transects illustrate that DWC speciation in the Gulf of Mexico is a function of depth and temperature. However, few studies have explored the potential importance of variations in bottom water dissolved oxygen (DO) and other chemical parameters on DWC community structure or function. Between June 2013 and May 2014, ROVs, AUVs, and submersibles equipped with multiple sensors obtained in situ measurements of DO, temperature, conductivity, pCO2, and turbidity in addition to discrete nutrient samples at 14 lease block stations ranging from the Florida Escarpment to the Louisiana continental slope that included oil spill impacted and non-impacted DWC communities. At DWC station depths ranging from 400 to 600 m, DO values within one meter of the seafloor were between 100 and 120 µM, values characteristic of the Gulf of Mexico's oxygen minimum zone. At stations below 700 m DO concentrations exceeded 170 µM. Localized production of dissolved inorganic nitrogen and dissolved organic carbon apparently stimulated by nearby DWC communities lacked an expected relationship to apparent oxygen utilization (AOU). Understanding controls on the distributions of coral species and influence of in situ chemical and physical properties on DWC communities may prove useful for models predicting the impacts of anthropogenic or natural hydrocarbon releases.

Persistent Effects of Ocean Acidification and Their Potential Synergetic Effects with Other Anthropogenic Disturbances

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Just as there are negative synergetic effects of temperature, nutrients, and ocean acidification on shallow-water corals, there may be significant synergetic effects of ocean acidification with other anthropogenic stressors on deep-water corals. Deep-water oil and gas development in the Gulf of Mexico often occurs in close proximity to sensitive biological communities, and resulted in significant impacts to deep-sea corals in the Deepwater Horizon incident. At depths between 300-600 m, Lophelia pertusa is the most common deepwater coral in the northern Gulf of Mexico, forming large reef structures that host a diverse associated community. Over the past 5 years, the carbonate system around these reefs has been exmained to provide a baseline for monitoring of the effects of ocean acidification. These reefs persist at an aragonite saturation state as low as 1.2, just above the saturation horizon and among the most adverse conditions ever recorded for a coral reef. The largest and most well-developed reefs are in the Viosca Knoll region, where the saturation state is somewhat higher, between 1.5 and 1.7. These are the closest reefs to the location where the Deepwater Horizon rig once stood, although they did not show obvious visual signs of impact. We argue that the higher saturation state around the Viosca Knoll reefs resulted in a greater baseline health of the corals, and that the corals to the west in the Green Canyon and Garden Banks areas may be less resilient to future impacts due to the lower saturation state of those waters.

Response and Resilience of Cold-water Corals to Anthropogenic Disturbance

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The Deepwater Horizon incident released an unprecedented amount of oil at depth in the Gulf of Mexico, with known adverse effects on deep-sea ecosystems and cold-water corals (White et al. 2012, Fisher et al. 2014). During the spill, dispersants were also applied at depth for the first time. The response of deep-sea organisms to both the oil and dispersant are not fully understood. Quantifying these effects on the surrounding communities is crucial to determining long-term environmental consequences at the species and population levels and informing future oil-spill response efforts. We conducted experiments on live corals at sea to investigate the physiological effects of surrogate oil and dispersant exposure on two deep-sea corals, *Callogorgia americana* and *Paramuricea biscaya*. We found that the dispersant-only exposure and the combined crude oil and dispersant exposures had a more pronounced effect on both coral species than crude oil treatments alone. In addition, RNA samples from impacted *P. biscaya* collected in 2010 from site MC294, as well as non-impacted areas in the GoM, were extracted and sequenced using Illumina RNAseq technology. This lead to the production of a de novo reference transcriptome, which we used to investigate possible gene expression changes in response to environmental stressors. Preliminary findings show an up-regulation of genes coding for cytochrome p450 & aryl hydrocarbon receptors in corals impacted during the spill. Our results provide insights into the responses of deep-sea corals to hydrocarbon and dispersant exposure, implications of applying dispersants to deep-sea oil spills and a novel reference assembly for a poorly studied group of corals.

Long-term Effect of the Deepwater Horizon Oil Spill on Corals and Associated Ophiuroids in the Deep Gulf of Mexico

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The 2010 Deepwater Horizon oil spill released more than four million barrels of crude oil directly into the deep Gulf of Mexico, potentially affecting mostly unknown deep-sea ecosystems. The first impacted coral community was discovered in late 2010, 11 km away from the Macondo well and at least two additional impacted coral communities were found in 2011. We digitized high definition images of coral colonies to follow the long-term effects of the oil spill. We also tracked the most common associate of these corals, the ophiuroid species Asteroschema clavigerum. Branch loss increased after 2011 with impacted branches being more likely to break, sometimes resulting in the loss of healthy portions of the colony. Using data from the last expedition, in June 2014, we can now measure growth rates in both impacted and non-impacted coral colonies. Ophiuroids responded quickly to the impact and were always observed on healthy portions of the colonies suggesting that they may be protecting part of the colony. The positive effect of ophiuroids on corals extended past twenty times the diameter of their central body disk. Although our last visit occurred four years after the oil spill, we are still observing changes in these long-lived organisms showing that the long-term consequences of the oil spill are still uncertain.

Potential Connectivity of Coldwater Black Coral Communities in the Northern Gulf of Mexico

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Leiopathes glaberrima is a black coral that represents a foundation species in the deep-sea benthos. Several cruises have contributed to map its 'spotty' presence in the northern Gulf of Mexico. Key characteristics of the species, such the longevity of its larvae and the timing of spawning, however, are presently unknown and hard to measure in-situ or in laboratories. Here the potential connectivity of *L. glaberrima* in the northern Gulf of Mexico is investigated using in combination a genetic and a physical model. The genetic analysis focuses on data collected at four sites distributed to the east and west of Mississippi Canyon. The circulation around the sites is simulated at a 1km horizontal resolution by a model of the ocean circulation with transport-tracking capabilities. Larvae are deployed 12 times over the course of 3 years and followed over intervals of 40 days. It is found that connectivity between sites to the east and west of the Canyon is hampered by the complex bathymetry and by flow instabilities at scales of few kilometers, that the interannual variability of the flow field surpasses seasonal changes, and that a competency period longer than a month is required for the simulated potential connectivity to match the low but detectable realized connectivity from multi-locus genetic data.

Three Stage Autonomous Underwater Vehicle Based Location of Deepwater Corals and Methane Seeps

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Methods for detailed study of benthic habitats continue to evolve; however, the basics were established several decades ago. Until recently a substantial barrier to conducting these studies was locating highly localized phenomena such as deep water corals or methane seep communities. Vessel based bathymetry, backscatter, and seismic data can suggest high probability regions but this often narrows the search to areas that are multiple to multiple tens of square kilometers. Since features of interest can range from a few meters for an isolated coral to a few tens of meters for a methane seep community, an efficient search method is required. A three stage methodology is presented for locating deep coral communities. This method starts with 3-d seismic data, followed by Autonomous Underwater Vehicle (AUV) based bathymetry and sidescan, and finally AUV based photography. This method was employed extensively in the immediate aftermath of the Deepwater Horizon incident. A similar three stage method for methane seeps is discussed beginning with vessel based multibeam water column data followed by AUV based sidescan and AUV based water column data, followed by AUV based photographs. This method was employed in a 2012 expedition to the Blake Ridge. These methods locate features of interest and simultaneously result in a synoptic view of the surrounding environment providing additional data about chemistry, macro fauna, geophysical, and physical oceanographic parameters.

Coral Injuries Observed at Mesophotic Coral Communities following the Deepwater Horizon Oil Discharge

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Pathologies in over 400 octocoral and antipatharian colonies were quantified in the aftermath of the DWH oil discharge at water depths of about 65 to 75 m offshore Mississippi and Alabama, Gulf of Mexico. A digital macro camera deployed from an ROV documented the coral communities of two sites: Alabama Alps Reef (AAR) and Roughtongue Reef (RTR). Observed taxa (identifications provisional), listed in order of injury frequency, included the following: *Hypnogorgia pendula*, *Bebryce spp*., *Thesea nivea*, *Swiftia exserta*, *Antipathes atlantica*, *Stichopathes sp*., and *Ellisella barbadensis*. The most conspicuous injury was a flake-like biofilm that covered branches. Extreme injuries featured bare skeleton and broken or missing branches. Comparing the 2011 results with previous photo surveys in the same study sites between 1997 and 1999, we find significantly elevated occurrences of injury over the historic levels and qualitatively different occurrences among taxa. Our findings indicate that coral injuries observed in 2011 resulted from an acute event rather than ongoing background processes. We hypothesize that Tropical Storm Bonnie facilitated and accelerated mixing of dispersant-treated hydrocarbons into the water column, resulting in harmful contact with coral colonies at mesophotic depths. Analysis of sediment PAH concentrations at AAR and RTR found levels elevated above pre-DWH discharge values, but well below toxicity thresholds established for fauna in estuarine sediments. The PAH concentrations measured in octocoral and echinoderm tissue samples from AAR and RTR were low compared to detection thresholds (10 - 100 ppb).

Decline in Condition of Sea Fans on Mesophotic Reefs in the Northern Gulf of Mexico before and after Deepwater Horizon Oil Spill

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Hard-bottom 'mesophotic' reefs along the ‘40-fathom’ shelf edge in the northern Gulf of Mexico were investigated for potential effects of the Deepwater Horizon (DWH) oil spill from the Macondo well. Alabama Alps Reef, Roughtongue Reef, and Yellowtail Reef were situated 60-90 meters below floating oil discharged during the DWH spill for several weeks and subject to dispersant applications. In contrast, Coral Trees Reef and Madison Swanson South Reef were far from DWH spill site, below the slick for less than a week or not at all, respectively. The reefs were surveyed by ROV in 2010, 2011, and 2014 and compared to similar surveys conducted one and two decades earlier. Gorgonian octocorals (sea fans) were present at all sites in moderate abundance. *Swiftia exserta*, *Hypnogorgia pendula*, *Thesea nivea*, and a yellow plexaurid were assessed for health in a BACI research design using still images captured from ROV video transects. Injury was modeled as a categorical response to proximity and time in an ordered logistic regression. Condition of sea fans at sites near Macondo well declined significantly post-spill. Before the spill, sea fans at sites near Macondo well were relatively pristine compared to reference sites. Injury was observed for 5-10% of large sea fans prior to the spill. After the spill, injury was observed in 27-34% of large sea fans. Odds of injury for sites near Macondo were 6.9 times higher post-spill, but unchanged at sites far. No new injuries occurred in healthy colonies marked in 2011 near Macondo well, but marked injured colonies declined in condition by 2014. Background stresses to

corals, including fishing activity, fishing debris, and coral predation were noted during surveys, but do not appear to account for changes near Macondo well.

Mercury Levels and Isotopic Composition in the Northeastern Gulf of Mexico: Geographical Variations in Hg Biogeochemistry and Bioaccumulation in Fish

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Mercury (Hg) pollution is a serious concern in the Gulf of Mexico (GoM) because of its toxicity and its ability to bioaccumulate in sea food, particularly in fish. Additionally, it is still unclear to what extent (geographical and temporal) the Deepwater Horizon oil spill in 2010 has perturbed the biogeochemistry and wildlife in the GoM. Here we report molecular and isotopic speciation of Hg in Tilefish caught in 2012 and 2013 along the shelf edge in the northeastern GoM, from the Mississippi estuary region to the head of the DeSoto Canyon. Fish caught close to both the Mississippi estuary and the wellhead of the DWH (<50 km) displayed significantly lower Hg levels and lighter isotopic composition than fish caught 150-200 km to the northeast. This clearly indicates differences in Hg biochemistry in the water column as well as different bioaccumulation efficiencies between those regions. We suggest that high particle discharge from the Mississippi River to the Gulf limits Hg bioavailability for the food webs, and that the oil and gas discharge potentially stimulated the development of micro-organisms involved in methyl-Hg degradation. Consistent with this scenario, the bioavailability of inorganic Hg to plankton and bacteria would be higher in offshore waters, leading to higher levels of MeHg in the food web and in predatory fish. The role of upwelling, bringing nutrient rich water to the surface, on Hg levels throughout the food web needs to be investigated. This study reveals that fish consumption advisories in the GoM should take into account that geographical variations in water chemistry and microbial populations can have an impact on MeHg production, so that the same species of fish can exhibit significantly different mercury concentrations.

New Data for Three Species of Hagfishes (*Myxinidae*) from the Northern Gulf of Mexico

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Hagfishes play important roles in the cycling of organic matter in deep-sea ecosystems through both scavenging and predation. This group also represents an ancient lineage of chordates that is of great interest to evolutionary biologists, yet very little is known about their basi biology and ecology. Three species of hagfishes are reported from the Gulf of Mexico (GOM), *Myxine mcmillanae* (Myxininae), *Eptatretus minor*, and *E. springeri* (Eptatretinae). Since the original species descriptions, very little has been reported on the biology or distribution of these species. Following the Deepwater Horizon oil spill, intense sampling of deep-water fishes in the northern GOM has yielded substantial specimen collections of these species. Specimens were collected during ten cruises in the northern GOM from 2011-2014 in depths of 397 to 1,156 m, with the two species of *Eptatretus* typically inhabiting shallower depths than *Myxine mcmillanae*. We will present morphometric and genetic data to verify the validity of each species. We will present the first data concerning depth ranges and spatial distribution for these species

as well as size distribution data and the first characterization of basic reproductive biology for each species. Finally, we will also discuss preliminary data regarding diet and methyl-mercury accumulation in these taxa. These data represent a considerable contribution to the knowledge of these understudied taxa.

Life History Characteristics of Two Common Deep-Water Dogfishes (*Squalus cubensis* and *S. cf. mitsukurii*) from the Northern Gulf of Mexico

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Determining the long-term effects of large scale, deep-water oil spills on fauna inhabiting the deep ocean requires an understanding of basic life history parameters for these organisms. In conjunction with the Deep-C project examining the ecological effects of the Deepwater Horizon oil spill, sharks were collected near Desoto Canyon in the northern Gulf of Mexico at depths of 191 to 2,645 m. Samples from 135 *Squalus cubensis* (SCUB) and 142 *S. cf. mitsukurii* (SMIT) were analyzed to determine reproductive and growth model parameters. Total length-based maturity ogives determined that sex-specific size-at-maturity varies considerably between these species (SCUB L50% maturity males (M)= 38.6 cm, females (F)= 47.8 cm; SMIT M= 54.4 cm, F= 66.2 cm). Both species were found to have concurrent ovarian cycles, and seasonal measurements of embryonic size distributions suggest seasonal mating for SCUB and aseasonal mating for SMIT. Fecundity ranged from 1-4 pups (x^{-} = 2.3 ± 0.68 SD) for SCUB and 5-10 pups (x^{-} = 6.6 ± 1.6 SD) for SMIT. Growth model parameters were estimated using multiple length-at-age models, with results suggesting conservative life histories characteristic of deep-water elasmobranchs. As the first reporting of age and growth for both species, findings will establish baseline data for subsequent comparative studies. Future research directions include continued monitoring of life history parameters to reveal any physiological effects of sustained pollutant exposure.

Session 015
Coastal Ecosystems Four Years after the DWH Oil Spill: What's Changed?

Oil Source Fingerprinting in Heavily Weathered Residues and Coastal Marsh Samples

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Oil source fingerprinting uses GCMS analyses of a source oil and environmental oil samples to try and match the chemical composition of key indicator compounds in both samples, thus providing strong evidence linking the environmental samples with suspected sources. These environmental samples are typically not heavily weathered, however, after a major oil spill, oil can travel for kms, and remain in coastal marshes and sandy beaches for many months to years. The compositional changes associated with weathering makes oil source fingerprinting challenging. This was especially true after the DHOS because the DHOS oil residues in some coastal areas may have a background petroleum contamination

from other spill events. We collected a large number of samples after the DHOS from nearshore coastal environments, including those after storm events. Samples were analyzed for the normal hydrocarbons (C10 to C35) and pristane and phytane and, several families of polycyclic aromatic hydrocarbons. The data was also generated for the oil biomarker compounds (hopanes, steranes, and triaromatic steroids). Because most of the samples were heavily weathered, the light aromatic hydrocarbons, as well as the normal saturate hydrocarbons, were either below detection limits or absent. As a result, oil source fingerprinting relied heavily on diagnostic ratios and patterns of hopanes, steranes, and triaromatic steroids (masses 191, 217, 218, and 231) and, on the relative compositions of three and four ringed parent PAH compounds and their C2 and C3 alkyl homologs compared to the sulfur containing analogues dibenzothiophene and naphthobenzothiophene. Data will be presented to demonstrate how these biomarker compositions were changed by weathering.

Impacts of River Diversions on Surface Oil Transport in Deltaic Gulf of Mexico Estuaries

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The extent and degree of shoreline oiling in the aftermath of the Deepwater Horizon oil spill have clearly shown that deltaic Gulf of Mexico estuaries are highly vulnerable to pollution from offshore oil spills. Yet, there have been few modeling studies dealing with oil transport in these systems. The implementation of 3-dimensional hydrodynamic models has been difficult because deltaic estuaries have extremely complex geomorphology and so numerical grids have to resolve both the complex bathymetry and intricate channel and wetland features. Modeling of estuarine-shelf exchanges is additionally complicated by the fact that estuarine residence times are strongly affected by pulsed freshwater discharges from man-made river diversions on the lower Mississippi River. Diversions are used primarily for salinity control but increasingly proposed also as a major way to deliver sediments and nutrients to coastal wetlands impacted by the construction of flood control levees. The impacts of river diversions on surface oil transport in Barataria and Breton Sound estuaries, the sites of the two largest freshwater diversion projects, were investigated using a high resolution, three-dimensional, Finite-Volume Coastal Ocean Model (FVCOM). The model was driven by tidal and subtidal forcing at the open Gulf of Mexico boundary, freshwater discharge from the diversions, and surface wind stress. We discuss some important challenges in developing oil spill trajectory models in these systems and evaluate tradeoffs associated with different Mississippi River management options.

A Temporal Study of an Alabama Salt Marsh Microbial Community Impacted by the Deepwater Horizon Oil Spill

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The Deepwater Horizon (DWH) oil spill in April 2010 released more than 200 million gallons of crude oil and approximately 2 million gallons of dispersants into the Gulf of Mexico. The primary objective of our temporal study is to provide a comprehensive understanding of the changes in the salt marsh microbial community structure and function during and after oil impacted the marsh ecosystem. Salt marsh sediments were collected from Point Aux Pines, Alabama beginning in June 2010 to December 2013. A metagenomic study of the indigenous microbial communities was conducted using high-throughput

methods such as PhyloChip microarrays, 16S rRNA amplicon and shotgun Illumina sequencing. Total nucleic acids were extracted from sediments during oiling of the study site in 2010 up to 2013. To the best of our knowledge, this study is the first temporal metagenomic-based analysis of microbial communities within a salt marsh impacted by the DWH oil spill. The results revealed an overall decrease in observed microbial species richness when oil was present at the site followed by a gradual increase in the years following the spill. Significant changes in relative abundance of known hydrocarbon-degrading groups were also observed in samples collected annually after the spill. The presence of oil at the site was also found to play an important role in microbial community structure within salt marsh sediments. In summary, these results contribute to our understanding of temporal variability in microbial communities, allowing us to detect patterns of distribution and predict microbial responses to changing environments and human-induced events such as the 2010 DWH oil spill.

Potential Impacts of Oiling on Nitrifying Communities in Louisiana Salt Marshes

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Recent studies have suggested that ammonia-oxidizing bacteria (AOB) and archaea (AOA) may have differential sensitivity to crude oil exposure. We investigated this hypothesis in communities of AOB and AOA in Louisiana salt marshes impacted by the Deepwater Horizon oil spill. Sediments were collected from oiled and unoiled sites from three regions between May 2012 until September 2013. Community composition was assessed by DNA fingerprinting (TRFLP) of ammonia monooxygenase genes (amoA) paired with DNA sequences from amoA gene clone libraries. In 2012, no differences were detected between oiled and unoiled sites in any of the regions, but strong regional differences were observed, with AOB communities in western Barataria Bay (WB) significantly different from communities in eastern Barataria (EB) and Terrebonne Bay (TB). In July 2013, AOB communities at oiled sites in western Barataria (WB) were significantly different from communities at unoiled sites. No significant differences in community composition related to oiling were observed in the other regions. Additionally, there were significant differences in AOB communities between July 2012 and July 2013 for all three regions. Interestingly, we did not detect any differences among AOA communities related to oiling. We did find significant differences in community composition of AOA and AOB at new sites in WB sampled in June 2013 from areas nearer the marsh edge. Our results suggest that AOB communities in WB are more sensitive to oil than AOB communities in eastern Barataria Bay or Terrebonne Bay and, in some cases, may be more sensitive to oil than the AOA communities in the marsh.

Ecosystem Responses to Changing Microbial Community Compositions as a Function of Natural and Anthropogenic Stressors in Louisiana Coastal Marshes

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Microbial community dynamics control salt marsh ecosystem diversity and function. Multivariate datasets from Spartina alterniflora marshes impacted by the Deepwater Horizon oil spill were evaluated to determine ecosystem response to natural and anthropogenic stressors. Sites were established by the Coastal Waters Consortium in 2012, and data include marsh edge and inland sediment and water physiochemistry, hydrocarbon measurements, and microbial and other faunal community assemblages.

From the data, S. alterniflora cover and plant height in the marsh correlated to total organic carbon (TOC) concentrations in the water and negatively correlated to dissolved oxygen (DO) levels. Lower plant height correlated to higher edge n-alkane concentrations, which also correlated to the relative abundances of Gammaproteobacteria, associated with organic matter degradation. These relationships among plant coverage and height, geochemistry, and microbial populations influence habitat conditions for higher trophic levels. For instance, *Adinia xenica* (Diamond killifish), usually from ponds and depressions, significantly and negatively correlated (according to Spearman's rho statistical analyses) to TOC, as well as to relative abundances of Epsilonproteobacteria, Actinobacteria, and Plantcomycetes. Ecosystem response, from primary productivity to faunal diversity and abundance changes, should become evident as the microbial community continues to respond to multiple stressors through time.

Sustained Impacts on Louisiana Salt Marsh Soil Greenhouse Gas Fluxes following the Deepwater Horizon Oil Spill

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We quantified the effects of the Deepwater Horizon oil spill on greenhouse gas (GHG) fluxes from oiled and unoiled Louisiana marsh soils. Temporal patterns were assessed along transects of increasing distance from marsh edges at 4 sites (2 unoiled, 2 oiled) in Terrebonne Bay (TB) over the 2012-2014 growing seasons. GHG fluxes showed significant seasonal and inter-annual (both in magnitude and seasonal patterns) variability. Oiled sites consistently had lower CO2 and N2O and higher CH4 fluxes 2 - 4.5 years post-exposure. CO2 was the major driver of soil radiative balance at all sites, but CH4 accounted for ~1/3 - ½ of forcing in oiled sites. CO2 fluxes increased with distance from marsh edge and increased with soil C, N and water content. CH4 fluxes increased and decreased with distance from marsh edge in unoiled and oiled marshes, respectively. Laboratory incubations of Barataria Bay (BB) soils associated with *Spartina alterniflora* and *Avicennia germinans* showed CO2 production was greater in unoiled marshes and comparable between vegetation types; CH4 production was greater in oiled marshes and *Avicennia* soils; N2O was higher in unoiled marshes and *Avicennia* soils. TB and BB marsh soils incubated at different salinities (5, 15, 25, 35 ppt) showed CO2 production increased and CH4 decreased with salinity; CH4 production was higher in TB and unoiled soils; CO2 production increased as the magnitude of salinity manipulation increased and the slope of the CO2 response to increased salinity was positively related to soil C, N and water content. These results have important implications for wetland carbon models and how fluxes may respond to both episodic (e.g., oil spills) and climate-related (e.g., altered salinity and vegetation) stressors.

Denitrification Rates in Marsh Sediments Exposed to Oil from the Deepwater Horizon Spill and Nearby Reference Sites in Louisiana Salt Marshes

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We investigated denitrification rates in Louisiana marsh sediments from 6 sites in Terrebonne Bay, Louisiana. Previously, there had been reports of oil on the marsh at some locations in the bay after the Deepwater Horizon spill, while other sites were not visibly oiled. We chose three locations where we could find oiled/unoiled pairs of sites near each other. Sediment cores were taken 10 m from the marsh

edge at each site for whole core measurements of denitrification using the isotope pairing technique. Additional samples were taken at both 1 m and 10 m from the marsh edge for potential denitrification measurements. Potential denitrification was determined using two different methods; by adding 15N-NO3 in sealed tubes and measuring the accumulation of 30N2 over 36 hours, and in a shorter term denitrification enzyme activity (DEA) assay. Previous measurements had found that potential nitrification rates increased with distance from the marsh edge in these Terrebonne marshes due to a change in elevation. We speculated potential denitrification might show the opposite pattern. Samples were taken in April, July and October. Preliminary analysis of the spring data suggests that sites nearest the edge exhibit more denitrification activity than sites at 10 m. Site to site variability was high making small differences difficult to detect. We did not see any obvious trends with oiling in the spring samples. Analysis of the July data, along with samples collected in October will provide a more robust measurement of differences between sites.

Rate and Trajectory of Erosion along the Louisiana Coast after the Deepwater Horizon Oil Spill

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Oil can have long-term detrimental effects on marsh plant health, both above- and below- ground. However, there are few data available that quantify the accelerated rate of erosion that oil may cause to the varying features of the coast and the trajectory of change. Between November 2010 and August 2012, we collected data on shoreline erosion, soil strength, percent cover of *Spartina alterniflora*, and marsh edge overhang at 30 closely-spaced low and high oil sites in Bay Batiste, Louisiana. We also used pre and post spill satellite imagery in oiled and unoiled locations along the Louisiana coast to estimate erosion rates over large areas. Results from both methods indicate that there is a threshold where soil parameters change dramatically with a relatively small increase in oil concentration in the soil. Heavy oiling weakens the soil, creating a deeper undercut of the upper 50 cm of the marsh edge, and causing an accelerated rate of shoreline erosion. Our results demonstrate that it could take years to document the effects heavy oiling has had on coastal erosion rates.

Landsat Detection of the Effect of the Macondo Oil Spill on the Southeastern Louisiana Coastal Marshes

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Increased rates of shoreline retreat of oiled marshes compared non-oiled marshes are one of the physical impacts of the Macondo Oil Spill on Louisiana's coastal marshes (Turner et al., in review). Using twenty-six Landsat (between 1984 to 2014) Thematic Mapper (TM) and two Operational Land Imager (OLI) data sets, we attempted to determine how widespread this effect was in Terrebonne Bay, Barataria Bay and Breton Sound saline marshes, in southeastern Louisiana. The location and extent of unoiled and maximum oiled marshes are based on compiled Shoreline Cleanup Assessment Techniques (SCAT) data (consisting of thin lines immediately adjacent to the coastline) downloaded from the ERMA Deepwater Gulf Response website for composite data sets from 2010 (http://gomex.erma.noaa.gov/erma.html). We imported the SCAT location data into ENVI and buffered by one pixel on either side of the SCAT line to form a 60 meter-wide buffer zone. Any marshland on the

August 29, 1984 data set that extended from the 60-meter buffer zone into the waters of the Gulf of Mexico was incorporated into the buffer zone. Ignoring minor inter-annual variations caused by varying tidal stage and winds, the data suggest an overall decrease in all marshes from shoreline retreat (indicated as a decline in marsh area) since 1984. While field evidence indicates differences in shoreline retreat between oiled and non-oiled sites, our preliminary results suggest they are not detectable with the 30 m2 spatial resolution of the two Landsat sensors. However, if the field-observed trends continue, then they will be become resolvable by Landsat, and much sooner by using more high resolution sensors.

Heavily Oiled Salt Marsh and the Deepwater Horizon Spill: Shoreline Cleanup, Emergency Restoration, and Ecological Recovery (2013-2014)

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The Deepwater Horizon oil spill resulted in persistent heavy oiling in salt marshes. Oiling conditions and ecological variables were compared among reference plots and three types of heavily oiled plots located in Barataria Bay: oiled control plots, mechanical cleanup plots, and mechanical treatment plots coupled with emergency restoration planting (*Spartina alterniflora*). Our 2013 data were collected more than three years following oiling and two years following cleanup and planting. Salt marsh oiling and associated impacts were apparent across all oiling/treatment classes relative to reference conditions. Mechanical treatment with planting showed the most improvement in oiling conditions and was also effective in re-establishing vegetation cover and species composition similar to reference conditions. *Littoraria irrorata* recovery was limited across all oiling/treatment classes. Impacts to *Uca spp*. were also documented in the heavily oiled plots. Positive influences of mechanical treatment and planting on invertebrate recovery were observed; however, recovery may lag the return of *S. alterniflora* by several years. Planting should be considered a spill response and emergency restoration option for heavily oiled marshes where vegetation impacts are substantial, natural recovery may be delayed, intensive cleanup treatments are used, or where marsh shorelines are at risk of erosion. Our presentation will include newly collected data from 2014, extending our study to more than four years following oiling and three years following cleanup treatments and planting. Our talk will feature updated results and interpretation spanning 2010-2014.

Effects of Oil-Contaminated Sediments on Wigeongrass (*Ruppia maritima*)

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Estuaries of the northern Gulf of Mexico contain a number of foundation species that provide nekton habitat, buffer coastlines from erosion, and provide various ecosystem services. The effects of oil inundation as a result of the 2010 Macondo spill, however, remain untested for many of these key species. Here, we discuss the implications of this spill for *Ruppia maritima*, one of the most common species of submerged vegetation in Louisiana and many other estuaries in the area. Specifically, we present the results of a greenhouse experiment where *R. maritima* was grown in a range of manipulated sediment oil concentrations: 0, 0.26, 0.53 and 1.05 mL oil /L total volume. We measured changes in

growth (wet weight, stem number/length), reproductive activity (flowering, fruits), and uprooting/breaking strength of plants after a 1 month period. While no difference was detected in growth, plants exhibited significant reductions in reproductive output and uprooting strength, with less flowers/fruits and force needed to uproot plants in medium and heavily oiled treatments. Given the importance of sexual reproduction for these plants, oil contamination may have substantial population-level effects. Moreover, plants may be more susceptible to high energy storm events due to the reduction in uprooting strength. Additional research is being directed at field verification of these trends and assessment of potentially less tolerant plants such as *Thalassia testudinum*.

Recovery of Saltmarsh Benthic Microalgae and Meiofauna after the Deepwater Horizon Oil Spill Linked to Recovery of *Spartina alterniflora*

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In salt marshes, benthic microalgae (a principal basal food resource) and meiofauna (a principal consumer of benthic microalgae and food resource to higher trophic levels) provide important ecological services in support of food webs. Here, we examine effects of the Deepwater Horizon Oil Spill in Louisiana salt marshes at three oiling intensities, and four years after the spill, compare recovery at this base of the food web with the recovery of the dominant marsh macrophyte *Spartina alterniflora*. Although impacts on the benthic microalgae and meiofauna were apparent at both moderately and heavily (in which plant mortality averaged nearly 100%) oiled sites, effects were strongest where plant mortality was highest. Five population and community metrics (microalgal biomass, photosynthetic pigment composition, the number of copepod species, meiofaunal community composition, and the density of meiofauna including nematodes, copepods, and polychaetes with larval dispersal) uniformly indicate recovery ~2.5 years post spill. Significantly, recovery was strongest at sites with moderate oiling where the stem density of recovering S. alterniflora was greatest, i.e., highest densities of meiofauna were observed where stem densities were highest. However for some taxa without larval dispersal (i.e., the sabellid polychaete *Manayunkia aestuarina*, kinorhynchs, and ostracods), recovery in heavy oiled sediment was much slower, just beginning after 4 years. These findings suggest that important ecological services provided by the benthic community in support of food webs return coincident with the recovery of *S. alterniflora*, and that *S. alterniflora* may be a good indicator for the broader recovery of the saltmarsh community.

Examining Spatial and Temporal Variation of Coastal Meiofauna Communities in the Northern Gulf of Mexico Using High-throughput Sequencing Approaches

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Meiofauna, which comprise of metazoan animals 45µm- 1mm that live between sediment grains, are important components of food webs and for nutrient exchange between the benthos and water column. Recent studies focused on these communities in the Gulf of Mexico due to potential impacts of the Deepwater Horizon Oil Spill (DWHOS). Intertidal meiofaunal communities from Mobile Bay and Dauphin Island, Alabama were previously shown to drastically shift from predominately metazoan taxa prior to DWHOS to a fungal dominated community after the spill. However, knowledge of variability within these communities remains unknown. We used Illumina high-throughput amplicon sequencing to examine

variation of coastal meiofauna communities. Sediment samples were collected bi- or tri-monthly from July 2011- July 2012. The meiofuanal community was examined by sequencing the eukaryotic hypervariable V9 region of the 18S rRNA gene. Results showed presence of fungal taxa, especially in intertidal locations, was limited. This suggests previously reported acute impacts of the DWHOS on meiofauna were apparently short term. However, these communities show shifts in proportions of metazoan taxa compared to pre-spill samples. Whether this change is due to prolonged impacts of the spill or variation in community composition is unclear. Continued sampling over a longer timeframe will provide a more complete understanding of seasonality and variation within these communities. Such a baseline is required to assess future anthropogenic impacts.

Recovery after the Deepwater Horizon Oil Spill: Response of the Macroinvertebrate Communities to Shoreline Oiling Effects

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The goal of our project was to examine the effects that shoreline oiling from the Deepwater Horizon event had on the macroinvertebrate community of the marsh, with these macroinvertebrates serving as proxies for marsh recovery over time. For two years we surveyed marsh periwinkles (*Littoraria irrorata*) as well as fiddler crab (*Uca spp*.) burrows, as these organisms are key indicator species of overall marsh health and both species have important influences on salt marsh ecosystem structure and function. Marsh periwinkles were divided into size classes (juvenile, sub-adult, and adult) to examine the size structure within sites and the possibility of new recruitment. Our sampling sites span Barataria Bay, LA, and represent areas of marsh shoreline classified as reference (no observed oil impact), moderately-oiled (some oiling observed), and heavily-oiled (significant oiling observed). Results thus far showed moderately-oiled sites to have the highest average density of *Littoraria* (93/m2, p-value = 0.00085). Also, an analysis of *Littoraria* size-class distribution across sites showed that, on average, heavily-oiled sites consisted of statistically smaller individuals (p-value = <0.001), possibly indicating that heavily-oiled sites are beginning to receive new recruitment from smaller, younger *Littoraria*, indicating marsh recovery. Post-release studies showed an initial response with a shift in fiddler crab species; however we found no significant trends and considerable variability. Our research will continue to monitor these sites over the course of the next two years.

Impacts of Oil Pollution on the Terrestrial Arthropods in Louisiana Saltmarshes: 2013 & 2014 Results

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Saltmarshes are one of the most productive ecosystems, supporting high abundance of different species. Terrestrial arthropods play an important role in the ecology of saltmarshes, affecting primary production and decomposition. Arthropods are often found in the gut contents of seaside sparrows and fishes making them an important tropic link to terrestrial and marine vertebrates. Though high diversity of arthropods are found in saltmarshes, they are understudied. Insects and spiders have the potential to be a good indicator of overall marsh health and environment as they are differentially sensitive to oil exposure. Oil pollutants may have significant long-term negative impacts on the terrestrial arthropods and consequently the food web. To determine the impacts of the Deepwater Horizon oil spill on the

Louisiana saltmarsh terrestrial arthropods, data from ten sites along the coast of Louisiana are included: 3 lightly-oiled, 4 heavily oiled sites in Barataria Bay, and 3 reference unoiled sites in Delacroix, St. Bernard Parish northeast of Barataria Bay. Insects were collected via sweep net, 20m inland from the shoreline monthly between April and June of 2013 and 2014. 28 families of insects were recorded. Hemiptera, Diptera, Orthoptera, Thysanoptera, and Araneae were the most abundant groups of arthropods found in most of the sites. Preliminary results combined with previous sampling at these sites show a significant decrease in the insect population on oil contaminated sites.

Seaside Sparrow CYP1A Gene Expression on Oiled and Unoiled Salt Marsh in Barataria Bay, Louisiana

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Following the 2010 Deepwater Horizon explosion, approximately 1,700 km of coastline was oiled, with approximately 45% of the oil coming ashore in salt marsh habitat, mostly in Louisiana (ca. 95%). Seaside Sparrows (*Ammodramus maritimus*) are an abundant terrestrial vertebrate in these salt marshes, and may serve as an important bioindicator of contamination affecting terrestrial organisms. To examine whether Seaside Sparrows were exposed to oil, we quantified the expression of a gene (CYP1A) that metabolizes certain toxic components of oil (polycyclic aromatic hydrocarbons; PAHs), using livers of birds collected over three years from replicated oiled and unoiled plots. Our results will indicate whether birds were exposed to PAHs in oil and how that exposure varied over time and space. Our results may also serve as an indication of how other terrestrial vertebrates, including humans, may have been affected.

Short and Long Term Effects of the Deepwater Horizon Oil Spill on Oyster Recruitment and Reef Biodiversity in Barataria Bay

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This study assesses both the long-term and acute response of oyster reef communities to hydrocarbon contamination and how the oil spill affected oyster recruitment. Four study sites were sampled in Barataria Bay: two control and two oiled, each with a low and high salinity location. Long-term effects on biodiversity were analyzed by quantifying faunal abundance, richness, and diversity from cultch-filled bags deployed at these sites in Barataria Bay. While abundance was generally greater at oiled sites, the effects of hydrocarbon contamination several years post spill were neither large nor consistent. To observe the acute response, oil-soaked and control bags were retrieved 1, 2, 4, and 8 weeks after deployment at Grand Isle, LA, in 2013. Oil effects on communities were inconsistent and minimal by week 8, perhaps due to biodegradation of the hydrocarbons. In 2012, spat recruitment on tiles placed at each site monthly varied more with salinity than oil contamination, but in 2013 early summer salinity was lower, and recruitment only occurred at the control sites. To study longer term effects on succession, cement substrates at each site were retrieved after 6, 12, and 18 months. Oysters reached smaller sizes at oiled sites, and curved mussels reached much higher densities at the low salinity, control site. In general our results suggest that oil contamination may interact with other stresses like low salinity to lower oyster recruitment, and that oil contamination may affect the density or size

distribution of estuarine bivalves over the long term, but perhaps not the invertebrate and fish community depending on them.

The Influence of Oil Exposure History and Population Genetic Variation on the Sensitivity of Gulf Killifish Embryos to Crude Oil

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Hydrocarbon exposure is known to interfere with the embryonic development of aquatic vertebrates, resulting in teratogenesis, impairment of cardiovascular development, reduced hatch, and reduced fitness upon hatch. However, most previous research has examined these developmental effects to oil exposure in fish embryos derived from brood stock with no previous history of oiling. There is, however, growing awareness that the genetic background or the hydrocarbon exposure history of fish can influence their sensitivity to organic pollutants. Few studies have considered the population genetic context when exploring mechanisms of toxicity and toxic sensitivity. This study will assess the sensitivity and biological effects of developing killifish embryos to exposure to water and sediments contaminated with southern Louisiana crude oil. Killifish embryos derived from six populations, ranging from Texas to Florida along the northern Gulf of Mexico, with different histories of environmental hydrocarbon exposure, were used in assays. Biological effects; including impairment in cardiovascular form and function, hatching success, larval morphometrics, and mortality; were monitored. Current studies are assessing the consequences of embryonic oil exposure on larval and juvenile fitness, including metabolic rate, hypoxia, and salinity tolerance. These data will provide important insight on the sensitivity of Gulf killifish from a broad range of habitats spanning the northern Gulf of Mexico.

Evaluating Otolith Microchemistry as a Method to Distinguish Habitat-Use Patterns in Marsh-Resident Fish

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Killifishes are dominant in marshes, play an important role in marsh food webs, and have limited home ranges. These characteristics make them useful as sentinel species. In particular, trace elements in killifish otoliths, may serve as a valuable indicator of the timing and spatial extent of exposure to oil. However, patterns of habitat use can vary among species, life history stages, and individuals. Therefore, when evaluating their potential as sentinel species, it is important to consider the temporal and spatial distribution of these highly localized fish within different marsh subhabitats (marsh edges, creeks, ponds, and depressions). Our recent work indicates the four most abundant killifish in Louisiana marshes are *Fundulus grandis*, *F. xenicus*, *Cyprinodon variegatus*, and *Poecilia latipinna*. While their abundance in ponds and depressions is high, only a small portion (<1%) occur along the marsh edge. Fish in these subhabitats can be exposed to varying levels of temperature, salinity, and trace metal concentrations. These three factors control the uptake of trace elements into the otoliths, an uptake that occurs in daily growth increments and provides a record of the fish's chemical environment. Our objective was to determine if otoliths of fish from different marsh subhabitats have distinct elemental signatures. The chemical compositions of 200 sagittal otoliths from these four fishes, collected across marsh subhabitats

near Chauvin, Louisiana, were analyzed. The levels of trace elements in recently-formed otolith rings were quantified using laser ablation with highly sensitive mass spectrometry. The ultimate goal of this study is to inform habitat-use patterns of marsh fish based on the chemical history of their otoliths.

Phytoplankton Responses to 2010 Deepwater Horizon Oil Spill

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Gulf of Mexico fisheries, accounting for 20% of the total United States Fisheries value, are supported by high phytoplankton productivity. Therefore, any disruption in phytoplankton productivity could result in a deleterious trophic cascade effect, crippling these important fisheries. The Deepwater Horizon oil spill may have disrupted northern Gulf of Mexico phytoplankton assemblages, and thus carried the potential to trigger a trophic cascade effect. This presentation will focus on the results of a study aimed to assess phytoplankton responses to crude oil and chemical dispersant in laboratory culture. Phytoplankton cultures were exposed to the water accommodated fraction (WAF) of Louisiana Sweet Crude Oil and the chemical dispersant Corexit EC9500A at high and low concentrations under different salinity and temperature regimes in order to determine phytoplankton responses to the toxicants. Culture health was determined by chlorophyll concentration, cell counts, and electron-transfer rate (ETR) between photosystems. Overall, phytoplankton were unaffected by oil WAFs but showed significant reduction in chlorophyll content, cell counts, and ETR when exposed to Corexit and Oil+Corexit WAFs. Furthermore, low temperatures and salinities increased the toxicity of the Oil+Corexit WAFs. These results suggest that phytoplankton assemblages, especially those nearshore and/or closer to riverine inputs, may have been impacted by the Deepwater Horizon oil spill, possibly resulting in a deleterious trophic cascade effect that would impact Gulf of Mexico fisheries.

Phytoplankton and the Macondo oil spill: A Comparison of the 2010 Phytoplankton Assemblage to Baseline Conditions on the Louisiana Shelf

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In this study, we report findings of a comparison between available baseline phytoplankton data from Louisiana coastal waters west of the Mississippi River (generally collected monthly between 1990 and 2009), and samples collected monthly from the same sampling stations between May and October 2010, during and following the Macondo oil spill. Our results indicate that overall, phytoplankton abundance was considerably lower following the Macondo oil spill, with diatoms and autotrophic dinoflagellates 38% and 68% below baseline conditions respectively. *Chaetoceros compressus*, *Thalassionema nitzschioides*, and *Dactyliosolen fragilissimus* were the three diatom species accounting for most of the decrease, whereas the autotrophic ciliate, *Mesodinium rubrum*, and the autotrophic dinoflagellate, *Heterocapsa niei*, were the other two members of the top five species that decreased in 2010. Heterotrophic microorganisms were similarly in lower abundance in 2010, with heterotrophic dinoflagellates and heterotrophic ciliates 60% and 14% below baseline conditions, respectively. Many aspects of this study are in agreement with studies of past oil spill events (e.g., suppression of some phytoplankton growth), although we did not find evidence of a stimulation of phytoplankton growth reported in some other studies. The lack of full agreement between this and past studies reaffirms

previous views that phytoplankton responses will vary according to the initial phytoplankton composition at the start of the oil spill, the specific composition of the spilled oil, and the season over which the oil was spilled.

The Effects of Nitrogen Loading and Low Oxygen Conditions on the Fate of Nitrogen in Coastal Ecosystems

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Excess nitrogen in coastal environments can lead to eutrophication, harmful algal blooms, habitat loss, oxygen depletion and reductions in biodiversity. As such, biological nitrogen (N) removal through the microbially-mediated processes of denitrification and anammox are critical ecosystem functions that help mitigate the negative consequences of excess nitrogen loading. Denitrification can release nitrous oxide, a potent greenhouse gas, as a byproduct under some environmental conditions. To understand how excess nitrogen loading impacts denitrification and anammox, we measured both processes in the water column of the Gulf of Mexico “Dead Zone”. The Dead Zone is generated by excessive nitrogen loading from the Mississippi River, which leads to a large summer-time hypoxic/anoxic area at the mouth of the river and along the coast of Louisiana. Rates of denitrification ranged from 24.5 to 244 nmol L-1 h-1, while anammox rates ranged from 2 to 8 nmol L-1 h-1. Maximal rates of both denitrification and anammox were observed at stations with the lowest oxygen concentrations. Waters exhibiting high rates of nitrate reduction also exhibited elevated concentrations of N2O, a potent greenhouse gas. Water column oxygen, sulfide, and dissolved organic carbon concentrations appear to interactively regulate rates of denitrification, anammox and N2O production within the Dead Zone’s waters.

Four Years after the DWH Oil Spill: What Has Changed with the Offshore Seaweeds and Rhodoliths in the NW Gulf of Mexico Deep Banks?

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Rhodolith (red algal nodules) beds offshore Louisiana in the northwestern Gulf of Mexico are associated with salt domes, unique deep bank habitats at 55-75m depth on the continental shelf. Sampling expeditions following the 2010 Deepwater Horizon (DWH) blowout to two rhodolith habitats revealed a drastic macroalgal die-off in locations that were diversity-rich pre-DWH. Laboratory observations showed macroalgal community regeneration from bare, apparently “dead” rhodoliths placed in 75-liter microcosms. These bare rhodoliths became gradually covered by a suite of algal germlings that were triggered to germinate, grow, and reproduce. Environmental sequencing of rDNA 16S (V4 region) and chloroplast-encoded tufA with Next-Generation sequence (NGS) analysis captured from within individual rhodolith microbiota revealed cryptic algal diversity spanning species to class level, presumably as overlooked spores, propagules, germlings and endolithic stages. A novel approach to link Sanger 16S sequences from “visible” algal stages collected pre-DWH and from post-DWH-regenerated specimens in our microcosms, with NGS of the “invisible,” hidden microbiota, realized a newly-found biodiversity assessment of cryptic algal communities that will lead to deeper understanding of far-ranging concepts

in life history evolution, biogeography, community cycling, regeneration and resilience in the marine environment.

Session 016
Dynamic Physical Processes in the Gulf of Mexico: What Have We Learned, What Does It Mean and How Can It Be Used?

Overview of the American Petroleum Institute (API) Joint Industry Task Force Subsea Dispersant Injection Project

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The American Petroleum Institute has sponsored research on subsea dispersant injection since 2011. The research is studying issues related to subsea injection of dispersant as a response to a deep water oil release. This information will be used to develop and communicate acceptable methods for implementing this technology to ensure its availablity both within the U.S. and internationally. Project teams are looking into all aspects of subsea dispersant injection including its effectiveness, fate and effects, and numerical modeling. As a result of this research, the body of knowledge regarding subsea dispersant injection has grown. Laboratory studies have demonstrated the utility of directly injecting dispersants at the source of a blowout. Testing has begun on the toxicity of a subsea plume to deepwater organisms. Additionally, progress has been made on enhancing numerical models to predict the fate of oil dispersed subsea. This presentation provides the scope of the project and preliminary results.

Circulation Patterns from the Surfzone Coastal Oil Pathways Experiment

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In December 2013 the Surfzone Coastal Oil Pathways Experiment (SCOPE) was conducted to examine the cross-shore exchange between the surf zone and inner shelf, 0-5km offshore. In situ observations of winds, water temperatures, salinities, waves, tides, and velocities measured over the water column were obtained to describe the surface and subsurface circulation forced by winds and waves, and the effect of a surface (<1m), buoyant plume along the Florida Panhandle. The plume originated from the adjacent inlet and had a westward-dominance that extended to the experimental site located 7km to the west. The Lagrangian particle behavior was estimated from 75 GPS-equipped drifters deployed between 0-5km offshore over a 5-day synoptic storm that induced winds from all directions. Significantly different drifter circulation patterns were observed that modified the drifter-derived surface dispersion and transport. The measured surface and subsurface flows often differed in magnitude and direction. In general, the surface flow is related to the local wind forcing, as pathline trajectories match coincident drifter trajectories. The drifter dispersion increased with decreasing wind speed and change in wind direction, and was enhanced by the presence of the buoyant plume. The

SCOPE experimental results of the Lagrangian and Eulerian circulation patterns and dispersion will be presented for a range of temporal and spatial scales.

Hurricane Isaac, Hercules Fire, and Winter Storms: The Gulf of Mexico Has It All!

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The diverse weather conditions in the Gulf of Mexico made it an ideal natural laboratory for observing and modeling physical processes affecting transport of pollutants and carbohydrate in the atmosphere marine boundary layer and the upper ocean. A comprehensive study is conducted using the University of Miami Coupled atmosphere-wave-ocean-land Model (UMCM) and observations from field programs. The model is configured with a multi-nested domain with gird resolution from 10km over the outer coarse domain to 400 m over the inner most domain. UMCM model simulations of transport in a wide range of weather conditions from hurricanes and winter storms to calm winds have been tested. Model results are compared with observations collected during Hurricane Isaac (2012) during GLAD, Hercules fire in July 2013, and winter storms during SCOPE in December 2013. It is found that the diurnal variability of surface winds and SST is dominant during Hercules fire event and in the winter storms, which is in strong contrast to hurricanes. Multi-scale downscaling from UMCM to LES models are important for better understanding transport processes. Transport is sensitive to the physical parameterization of turbulent mixing and wind-wave-current coupling in UMCM. In situ observations and high-resolution coupled modeling together is a key to advance our knowledge and capability in predicting transport of pollutants and carbohydrate, which is the perhaps most important thing we have learn so far.

The Nature of Surface Ocean Transport in Realistic Simulations of the Gulf of Mexico

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We apply the recent geodesic theory of Lagrangian Coherent Structures (LCS) on high (1 km) and very-high (0.25 km) resolution model simulations of the Gulf of Mexico. We find that passive tracers on the surface of the ocean in those simulations develop conservative-looking patterns that are largely consistent with those produced by an incompressible two-dimensional velocity field. We discuss the implications of this finding.

Coastal Circulation during SCOPE from Satellite Remote Sensing

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With GoMRI RFPII support, the Center for Southeastern Tropical Advanced Remote Sensing (CSTARS) at the University of Miami collaborated with the CARTHE consortium to provide satellite imagery for the Surfzone Coastal Oil Pathways Experiment (SCOPE). The goal of this experiment, conducted from December 2 to December 19, 2013 near Ft Walton Beach, FL, was to observe the cross-shore exchange

of material between the inner shelf and surf zone. CSTARS obtained 24 SAR images from the Cosmo-SkyMed constellation, TerraSAR-X, and RadarSat-2; as well as 11 optical images from RapidEye and EROS-B. Some are of poor quality due to weather, but most provide unprecedented observation of the coastal circulation features which drive oil trajectories near shore. On several days, fronts were identified in the morning SAR imagery and subsequently observed about 6 hours later in the optical imagery, permitting the speed at which the fronts propagate along the coast to be calculated. Surface drifting buoys released during SCOPE frequently collected along frontal features observed in the SAR images, indicating that the fronts are convergence zones. These features were observed in the coastal zone as well are further out over the continental shelf. The fronts were sampled extensively in situ by CARTHE. Together, the satellite imagery and in situ sampling provide an unprecedented three-dimensional view of the controlling mechanisms for transport at the sea surface. Implications for understanding current-driven oil dispersal are discussed, and new methods to further exploit SAR satellite imagery for oil spill mitigation are presented.

Near-bottom Response to Tropical Cyclones in Regions with Steep Bathymetry

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Great attention has been given to the upper ocean response to tropical cyclones (TC), focused on air-sea interaction that may impact TC intensification as well as surface currents and waves that may impact offshore structures and potentially transport surface pollutants. Less attention has been paid to the ocean response at depth, particularly below the surface mixed layer. Analysis of recent and historic observational data has yielded evidence of potentially strong near-bottom currents at depths exceeding 1000m or more. Numerical simulations conducted for historic storms show that these strong currents may be trapped to steep topographic features, such as the west Florida Escarpment and rim of the DeSoto Canyon region, areas of active or potential future oil and gas exploration and extraction. These currents, though likely localized in space and occurring infrequently, may potentially have critical impacts on near-bottom structures such as pipelines and risers, and may also be important for resuspension and transport of oil spill-related materials deposited on the sea floor. In this work, high-resolution numerical simulations of historic storms in the DeSoto Canyon and other regions of the Gulf of Mexico are conducted using a model configured to resolve near-bottom currents over complex bathymetric features. Analyses of the model and observational data characterize the spatio-temporal variability of the near-bottom currents, the genesis mechanisms of these currents, and importance of topography.

Characterization of the Uncertainty of Loop Current Metrics using a Multidecadal Numerical Simulation and Altimeter Observations

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Satellite altimetry is routinely used to monitor Loop Current intrusion and eddy shedding in the Gulf of Mexico. Statistical estimates of the location and variability of the Loop Current vary significantly among published studies and it is not obvious whether these differences are caused by observational errors, different analysis methodologies, processing and gridding of altimeter data products, or the highly irregular nature of the Loop Current system itself. This study analyzes the uncertainty of basic Loop

Current statistical estimates derived from altimeter observations, i.e. the northern and western extent, the mean Loop Current eddy separation period, and the relationship between the Loop Current retreat latitude and eddy separation period. The robustness of these statistics is assessed using sea surface height data from a 1/25° free-running multidecadal numerical simulation of the Gulf of Mexico HYbrid Coordinate Ocean Model. A suite of sensitivity tests is performed to identify sources of uncertainty in the Loop Current statistics. The tests demonstrate that the Loop Current metrics from the altimeter fields are less sensitive to the choice of the reference sea surface height mean field or Loop Current front definition than to satellite sampling patterns. Stationarity of the LC system is also analyzed. The mean separation period estimated from the altimeter fields for 1992-2010 is 8 months with the 95% confidence interval (6.1-9.8) months.

Lagrangian and Eulerian Observations of the Transport Induced by Wind, Waves and Tides near the Sea Surface

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Where the uppermost layer of the ocean meets the atmosphere, it is notoriously challenging to measure, or even define, what the "surface velocity field" would be. Though this understanding is necessary in order to better predict the variety of observed oil spills trajectories and behaviors. Here we present a series of experiments where we observe, combining Lagrangian and Eulerian methods, the transport of near-surface material subjected to surface processes such as Stokes drift, windage, tides and local stratification effects. Each experiment, executed across many sea states, consists of a set of deployments of a cluster of surface drifters of different drafts sampling different depth between 0.2m and 1.5m. Each deployment lasted over 10 to 60 minutes in order to avoid decorrelation of the trajectories by entrainment of the drifters into different coherent structures. Among these drifters are several generations of our new design, but also drifters previously used during large deployments coordinated by CARTHE, as well as commercially available designs (e.g. the iSphere and the MicroStar). The surface winds, ranging from 0.5 m/s up to 12 m/s, were recorded locally and compared to near-by coastal NOAA stations. The surface Eulerian currents were measured at high resolution with a surface-mounted, pulse-coherent current profiler. The wave statistics were estimated combining GPS and accelerometer sensors data from Wave Resolving Drifters (WRD) released with every trial. We also conducted periodic CTD casts during the launches to monitor the local stratification. The analysis of this data allows us to evaluate our new design and to study the effects of various surface processes on surface transport.

The Effect of Wind, Baroclinic Instabilities, and Shelf Circulation on the Cross-shore Transport of Surface Materials

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Coastal currents in the northern Gulf of Mexico are driven primarily by local along-shore wind forcing. Near the coast, buoyancy forcing can shift this response by generating an additional along-shore current forcing. Further offshore, the Mississippi/Atchafala River plume responds to winds as an Ekman layer; winds shift the plume position and the transport of materials carried by the plume. Therefore, upwelling and downwelling winds can either inhibit or enhance surface oil slicks interaction with the coastline. In

the northern Gulf of Mexico, the Mississippi/Atchafalaya river plume is also associated with strong, energetic eddies caused by baroclinic instabilities in the plume front. These eddies can enhance the cross-shore dispersion of an oil slick, enhancing potential interaction of a slick with the coastline. The relative importance of each of these processes could be estimated by a linear superposition, except that winds may also affect the nature of the shelf eddies. The nonlinear coupling between Ekman transport of the plume and shelf eddies, as it relates to cross-shore transport of materials is examined by using a realistic, validated hydrodynamic model of the norther Gulf of Mexico, along with a series of idealized experiments. The realistic model is based on an operational hydrodynamic model used for oil spill response. The idealized model is used to represent a range of conditions similar to those observed over the Texas-Louisiana shelf during summertime. Simulations are analyzed using numerical surface drifters, to represent oil transported in the near-surface ocean. These simulations provide a better understanding of cross-shore transport of surface materials in the context of coastal impacts of oil spills.

Coastal Models of Oil Transport in the Northern Gulf of Mexico

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Transport forecasts require physics-based computational models and high-resolution meshes that represent the waves, tides and circulation in deep water, on the continental shelf, and within the complex nearshore environment. This work applies the ADCIRC coastal circulation model with a Lagrangian particle transport model to simulate the three-dimensional transport of oil in the Gulf of Mexico. Baroclinic initial and boundary conditions for ADCIRC are provided through a coupling with NCOM. The transport model accounts for the source of oil at the wellhead; advection due to tides, riverine discharge, oceanographic currents, meteorological forcing and breaking waves. Transport is validated against available measurements, including drifters released during the Surfzone Coastal Oil Pathways Experiment (SCOPE) conducted by CARTHE. It is shown that the increased mesh resolution near the coast does improve the simulated transport into the nearshore.

Impact of Submesoscale Processes on Mean Circulation, Transport and Mixing in the Deep Waters of the Northern Gulf of Mexico

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The circulation and variability of the northern Gulf of Mexico are investigated using a regional ocean model (ROMS) and two-way nesting techniques to compare results at two horizontal resolutions, 5 km and 1.6 km, over a three year period, from January 2010 to December 2012. We focus on the representation of processes and instabilities below the mixed layer. Submesoscale eddies and vorticity filaments populate the continental slope, where mean currents are weak compared to the eddy kinetic energy contribution. A dipole formed by the interaction of the mean currents with the Mississippi Fan foldbelt dominates the mesoscale eddy field below depths of about 1000 m. The mesoscale and submesoscale eddy field along the slope intensifies with horizontal resolution, as quantified by local energy conversion terms. Furthermore, the mean energy distribution of the water column is altered by the model resolution. Increasing resolution results in an intensification of the mean circulation at depths greater than ~ 1000 m of about 30-40%, and a corresponding weakening of Loop Current in the upper layer, at depths comprised between the base of the mixed layer and 1000 m. The representation of the

Loop Current is in better agreement with the available observational constrains in the 1.6 km run. Those mean flow differences have broad implications for the representation of horizontal and vertical transport in the two modeled flows and for any future forecasting effort in the event of deepwater oil spills. With a series of passive tracer integrations we quantify the role played by submesoscale dynamics in the maintenance and spread of deep tracer plumes, and we diagnose the lower vertical diffusivities that characterize the nested solution.

Improved Surface Transport Estimates in the Gulf of Mexico by Blending Altimetry and Drifter Data

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Estimating transport by surface currents is central for oil spill mitigation and accurate measurements of the ocean velocity field are essential for this purpose. In this work we investigate how to improve altimetry-based surface geostrophic currents, that are necessarily limited by satellite tracks distance and resolution, by blending them with drifter (local) information. Since drifters directly sample transport in the upper ocean at various scales, they are expected to restore the velocity field variability at space and time scales that cannot be sampled by the altimeter, while introducing also ageostrophic components that cannot be simply described through Ekman component superposition. The extensive GLAD (Grand LAgrangian Deployment) drifter data set in the Gulf of Mexico is blended with AVISO-based geostrophic fields via LAVA (LAgrangian Variational Analysis). Hindcast trajectories from AVISO-based geostrophic velocities provide satisfactory average results (skill score S>0.4) in open ocean mesoscale structures. In regions with smaller scale dynamics, such as the DeSoto Canyon and the shelf, altimeter skill score is reduced. The total average distance D between hindcast and drifter trajectories is ~45 km after 3 days, slightly less than the distance D0 covered by the drifters. Blending information from a subset of drifters leads to a significant improvement in all the dynamical regions, with S typically higher than 0.8 and D reduced to less than half of D0.

Richardson Pair Dispersion in the Surface Ocean

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Using two-point velocity and position data from the near-simultaneous release of O(200) GPS-tracked surface drifters in the northern Gulf of Mexico, we examine the applicability of classical turbulent dispersion laws to upper ocean velocity fields. The data set allows direct estimates of velocity structure functions and the temporal evolution of the distribution of particle pair separations. On 100m-10km spatial scales, and time scales of order 1-10 days, all metrics of the observed surface turbulence are consistent with standard Kolmogorov-Kraichnan theory for two-dimensional turbulence in the energy cascade regime, including the existence of an inertial range with a defined, scale-independent, dissipation rate. Self-similarity of the observed particle pair distributions shows strong agreement with Richardson's law. The observed submesoscale pair statistics compare remarkably well to those produced

in controlled, laboratory-scale experiments of two-dimensional turbulence in the inverse cascade regime.

Trapping Heights in Hot Multiphase Plumes

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An essential characteristic of stratified, multiphase plume is the possible presence of multiple lateral intrusion levels where transported quantities accumulate and spread in the horizontal. Predicting these trapping heights has been the focus of considerable effort. In most experimental studies, plumes are driven by density differences between the injected phase and the bulk liquid. As such, the fields contributing to the inlet buoyancy flux, B, are not those responsible for setting the ambient stratification (`cold' plumes). In contrast, deepwater blowouts in environments stratified by temperature differences typically involve significant thermal contributions to $B$ (`hot' plumes). Using classic plume scaling, with frequency N and velocity $U=(BN)^{1/4}$, experiments confirm that the trapping height is given by $h_t = f U/N$ where the coefficient f depends on the entrainment factor and the ratio w_s/U of the phase slip velocity to the velocity scale. Here we use turbulence resolving simulations to study the differences in trapping heights between cold and hot plumes. The computational model is validated by direct comparison to experimental results for cold plumes showing excellent quantitative agreement for the parameter dependence and size of f. Simulations of hot plumes indicate significant reductions in intrusion heights due primarily to enhanced turbulent mixing of temperature. An extended oil-gas-temperature model, at parameter values similar to those of the Deepwater Horizon spill, predicts intrusion heights in agreement with indirect, in-situ concentration measurements.

Texas and Louisiana Coastline Sensitivity and Oil Dispersion

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Knowledge of where spilled oil will travel is enhanced by improved understanding of transport properties in the region of interest. Using a numerical model of the Texas and Louisiana shelves combined with a Lagrangian trajectory model, we have calculated the dispersion characteristics of the region. The dispersion tells us how quickly material - for example, oil tar balls from a spill - from different areas will be transported away by the ocean currents. We have found that dispersion is larger in the northern shelf area, especially Louisiana, during the summer months as compared with the winter. We have also measured coastal connectivity to assess likely impacts to the shoreline; that is, in what areas a spill could occur that would then be likely to travel to the coast. We find strong seasonal differences in the connectivity; in some cases we also find interannual variation. For example, the areas of the shelf that are connected with the south Texas coastline are different in the summer and the winter, and this pattern also varies somewhat interannually; however, transport to the western Lousiana coastline is almost nonexistant in the winter in all of the seven years studied. Using these results, future spill responders could focus their efforts on coastline areas that are more likely to be affected, based on the time of year and location of the spill. Additionally, as a spill spreads, responders could focus on areas with higher dispersion rates as opposed to those in which material transports away more slowly.

Physical Processes Controlling Tracer Exchange at the Mouth of Galveston Bay

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Predicting the long-term distribution of a tracer in an estuary ultimately requires understanding the physics of the exchange flow at the mouth of these systems. We have developed a three-dimensional unstructured grid hydrodynamic model of Galveston Bay to explore how the estuary responds to changing river discharge, tides, atmospheric conditions and coastal circulation. By comparing different model grid resolutions and topologies, the model highlighted that resolving ~100 m bathymetric features was necessary to correctly reproduce long-term observations of a tracer; salinity in this case. The model representation of fine scale velocity gradients generated by the tidal interaction with the topography was ultimately the cause of different levels of tidal exchange and hence salinity predictions within the bay. Numerical modeling of many months of realistic conditions has taught us that Galveston Bay, and likely many other Gulf coast estuaries, are highly unsteady systems that are in a constant state of adjustment to variable forcing conditions. Classical steady state formulae for predicting salinity are therefore not applicable in these regimes and instead we present a simple analytical framework for handling the unsteadiness. These lessons learned from the modeling will aid in improving predictions of how other tracers, such as oil and chemical pollutants, will respond to changes in estuarine forcing.

Atmospheric Turbulent Structure and Vertical Transport in the Hurricane Boundary Layer

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Hurricane boundary layer (HBL) processes, especially, the structure of the coherent large eddy circulations (LECs) and their induced vertical transport, are not well understood. In this study, a large eddy simulation (LES) in a weather hindcasting mode, which is driven by UM's fully coupled simulation of Hurricane Isaac, is used to investigate the atmospheric turbulent structure and vertical transport in the HBL. It is the very first time that an LES successfully includes a responsive ocean so that LECs in the HBL can be realistically simulated. The simulation shows that the HBL LECs exist in a mean stable environment and consist of well defined updraft and downdraft. Statistically, the HBL LECs are only slightly skewed with the updrafts and downdrafts relatively evenly distributed spatially. The weak inversion base of the HBL basically envelopes the upper boundary of LECs. The trough in between two adjacent LECs is where most entrainment takes place, whereas the crest of the LECs is where the air detrains out of the HBL. In such a way, LECs directly connect the surface, the HBL, and the main body of a hurricane vortex and enhance the exchange of energy, moisture, and momentum between them. It is found that the current boundary layer schemes significantly under-estimate the resolved turbulent fluxes due to the fact that the effects of LECs have not been included in the parameterizations. This study also investigates different instability modes, such as inflection-point instability, convective instability, and parallel instability, in the strongly sheared environment of HBL.

The Role of Turbulence on Droplet Dynamics: Application to the Deepwater Horizon Oil Spill in the Gulf of Mexico

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An integrated observational field effort that makes direct measurements of turbulence has been conducted near the Deepwater Horizon oil spill site in the GOM. Full water column profiles are collected across the continental slope in summer 2013 and 2014. TKE dissipation rate is estimated from velocity shear spectra or micro-temperature spectra. The observational results suggest that strong turbulence is patchy and mostly measured in the thermocline and deepwater when using the buoyancy Reynolds number, Reb =200 criterion, the boundary between weak and strong turbulence. Bottom enhanced turbulence is often seen on the continental slope. Using the ratio of the turbulent velocity scale and the oil droplets rising velocity, we develop criteria for when turbulence will dominate the movement of oil droplets and when turbulence can be ignored. Based on the data collected, for oil droplets with rising velocity greater than 6×10^-3 m/s, the turbulence effect can be ignored on the continental slope of the northern GOM. For oil droplets with rising speed less than 10^-4 m/s, they will passively move with the turbulent flow at all depths. For oil droplets with rising speed between 10^-4 and 6×10^-3 m/s, the role of turbulence will depend on the strength of the local turbulence and water stratification. We also relate turbulent velocity to the size and density of oil droplets by estimating the rising velocity of different size oil droplets due to balance between buoyancy and drag force. Droplet size and density are the two critical parameters in determining the role of turbulence. When the density difference is small (1 kg/m^3), droplets with size less than 6 ×10^-3 m will likely be captured by the strong turbulent flow and become passive Lagrangian tracers.

Large-eddy Simulation and K-profile Parameterization of Oceanic Oil Spill Dispersion

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As oil plumes from underwater blowouts reach the ocean mixed layer, their near-surface dispersion is influenced heavily by wind and wave-generated Langmuir turbulence. In this study, the complex oil spill dispersion process is modeled using large-eddy simulation (LES). The mean plume dispersion is characterized by performing statistical analysis of the resulting fields from the LES data. Although the instantaneous oil concentration exhibits high intermittency with complex spatial patterns, it is found that the time-averaged oil distribution can be parameterized as a Gaussian-type plume. Many key characteristics of the mean oil plume are found to vary monotonically as a function of the drift-to-buoyancy ratio Db=Us/wr, where Us and wr are the Stokes drift velocity and droplet rise velocity, respectively. The smoothness of the mean plume makes it feasible to simulate the oil dispersion using Reynolds-averaged type formulations, such as the K-profile parameterization (KPP). Using LES data, we evaluate the eddy viscosity and eddy diffusivity following the KPP framework. We assess the performance of previous KPP models for pure shear turbulence and Langmuir turbulence by comparing them with the LES data. Based on the assessment an improved KPP model is proposed, which shows much improved overall agreement with the LES results for both the eddy viscosity and the eddy diffusivity of the oil dispersion for a variety of flow conditions and droplet sizes. This study is supported by a Gulf of Mexico Research Initiative RFP-II research grant.

Seasonal Variability and Robustness of Two-particle Statistical Measures in a Very-high-resolution simulation of the Northern Gulf of Mexico

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Lagrangian statistics are investigated using synthetic trajectories produced by the surface ocean velocity output from a very-high (250 m) resolution model simulation of the northern Gulf of Mexico. Various separation measures are considered and a comparison with Eulerian structure functions is conducted. The seasonal dependence of these measures and the sensitivity to the amount of data involved in their calculation are investigated.

Identification of Bottom Intensified Dynamics on the Northern Gulf of Mexico Slope and Their Impact on Fate and Transport Modeling

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The so-called “Smooth Orthogonal Decomposition” technique is applied to an oceanographic dataset. This decomposition technique overcomes some limitations of other orthogonal decomposition techniques by identifying those modes that behave smoothly in time and thus being sensitive to both variance amplitude as well as frequency. This important property is demonstrated through identification of a bottom intensified four-day topographic Rossby wave on the Louisiana slope. This is a significantly higher frequency wave than previously thought to exist in the region. The above finding represents the importance of bottom-intensified dynamics on the northern Gulf of Mexico slope. Observations from the GISR mooring array (2-year deployment near 28.5N 88.5W) suggest that the bottom boundary-layer in the vicinity of 27N 92.5W is governed by the Froude number 1, Rossby number 1 parameter regime. This may explain a region of accumulation identified by a one-year deep tracer release experiment, conducted over the northern Gulf of Mexico slope, which was not well-represented by numerical modeling efforts. To begin accounting for this discrepancy a barotropic analytic solution for flow over variable slope topography is proposed. This analytic solution represents a situation in which the structure and stability of the bottom boundary-layer governs the interior water column dynamics, and is thus a significant consideration for fate and transport modeling. GoMRI funded publications: Kuehl, et al. (2014). Application of the Smooth Orthogonal Decomposition to oceanographic datasets. GRL, 41 (11). Kuehl (2014). An analytic solution for barotropic flow along a variable slope topography. GRL, under consideration.

Session 017
High-Pressure Experimental and Modeling-Based Studies for Understanding Deep Blowout

Gas Hydrate Formation in Deep Ocean Conditions

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Gas Hydrates are crystalline inclusion compounds formed from water and gas at high pressures and/or low temperatures. These temperature and pressure conditions are found in the deep ocean and during a deepwater oil spill/gas blowout, thereby leading to hydrate formation around gas bubbles and oil droplets. Advancing our understanding of gas hydrate formation under these deepwater conditions is critical to the safe and efficient containment of an oil spill as well as to help mitigate the environmental impacts of such an event. This presentation will provide an overview of the hydrate science related to the formation of hydrates in deepwater ocean conditions, including the formation of hydrate encrusted gas bubbles and water/oil droplets.

An Integrated Approach for the Experimental Investigation of Hydrocarbon Jet Behavior under Artificial Deep-sea Conditions

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The experimental investigation of gas-and-oil jets in the deep sea is a multifaceted problem. It consists of the behavior and properties of each single hydrocarbon particle, the interaction of these particles and the evolution of both particles and interactions over time and space. In order to achieve an integrated model of the behavior of such a jet, each of these aspects must be addressed. For this purpose, an integrated experimental approach using a family of test modules at deep sea conditions (high pressure, low temperature) was developed at Hamburg University of Technology. By addressing each aspect of the jet separately in a specialized setup, they can be investigated at a higher level of detail and thereby yield a higher certainty of cause and effect. The Jet Modules I to III of this family are used for the investigation of rising velocities of hydrocarbon particles (gas bubbles, live and dead oil droplets, solid gas hydrates) with diameters from 100 µm to 5 mm and particle size distributions of scaled gas-and-oil jets (diameter range: 30-1500 µm). The data gained from these modules covers the aspects of single particle behavior and particle interaction. In this work, two new modules are presented for long-term investigations of the mass transfer and evolution of hydrocarbons in the ocean. The rise of both single particles and emulsions from sea floor to surface is simulated by adjusting pressure and temperature over time in accordance with their movement through the water column. Those new modules add the aspect of evolution over time and space and thereby complete the integrated experimental model of a deep sea jet.

Oil Droplet Size Distribution and Fluorescence in Subsea Plume Simulations: Implications for Response Tools

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Optical measurements have been used during oil spill response for more than three decades to determine oil presence in slicks and plumes, and on shorelines. Oil surveillance ranges from simple (human eyeball) to the sophisticated (sensors on AUVs, aircraft, satellites), where SMART protocols provide guidance for visual detection and fluorometry during spills. In situ fluorometers and particle size analyzers were deployed during the Deepwater Horizon (DWH) Gulf of Mexico oil spill to track shallow and deep subsea plumes. Uncertainties regarding instrument specifications and capabilities necessitated performance testing of sensors exposed to simulated, dispersed oil plumes. Presented here are results of wave tank experiments conducted at the Bedford Institute of Oceanography. Examined were simulations of subsea releases with varying parameters such as oil release rate, oil temperature (reservoir temp ~ 80 ^{o}C), water temperature (<8 ^{o}C and >15 ^{o}C), oil type, and dispersant to oil ratio (DOR). Plumes of Alaskan North Slope Crude, South Louisiana Crude and IFO-120 were tracked using in situ fluorescence, droplet size distribution (DSD; LISST 100X), total petroleum hydrocarbons (TPH), benzene-toluene-ethylbenzene-xylene (BTEX) and excitation-emission matrix spectroscopy. Findings have implications for fate & transport models, where DSD, chemistry and fluorescence are all impacted by release variables. Research supported by the Bureau of Safety & Environmental Enforcement.

Gas Plume Bubble Dissolution at Gulf of Mexico Natural Methane Seeps

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Bubble dissolution is one of several processes that influence the transport of volatile hydrocarbons from natural gas seeps and anthropogenic releases. Within the hydrate stability zone, dissolution rates are influenced by the presence of hydrate skins on bubbles. We collected water samples from gas plumes and measured dissolved methane concentrations shipboard during a recent cruise to Green Canyon and Mississippi Canyon methane seeps to improve our understanding of bubble dissolution. Samples were collected by remotely operated vehicle in vertical profiles following bubble streams from the seafloor up to 200 m above bottom. Samples were also collected at constant depth, 100 m above bottom, in horizontal transects across a bubble plume. These samples were co-located with measurements of bubble physical properties derived from high-speed videography. The measurements reveal significantly elevated dissolved methane within gas plumes indicating quantifiable dissolution despite evidence of hydrated bubbles. At 100 m above bottom, the transfer of volatile hydrocarbons from bubbles to the dissolved phase was sufficient to reach dissolved methane concentrations >15 µmol L-1. Immediately outside the bubble field, dissolved methane concentrations attenuated rapidly to background. Dissolved methane concentrations at the seepage source were significantly greater. These field data are being used to validate models of bubble plume dissolution.

Effect of Gas Hydrates on the Fate of Rising Hydrocarbon Bubbles from Natural Seeps and Accidental Releases in the Deep Ocean

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Hydrocarbon gases released in the ocean undergo physicochemical processes as they rise through the water column. The fate of bubble depends on its rise velocity and dissolution rate, which are known to decrease as the gas-water interface becomes contaminated in natural waters. Especially at the high pressure and low temperature, the interface may become coated by a hydrate shell, which may interfere with the gas exchange between the bubble and ambient. Thus, to accurately predict the fate of gas bubbles released from seeps or accidental spills in the deep ocean, it is important to understand the effect of hydrates on the mass transfer and rise velocity of bubbles. In this study, a numerical model is developed to estimate the behavior of gas bubbles. We use the Lagragian approach to track the pathways of transforming bubbles, accounting for local dissolution and rise velocity. Our model applies the standard mass transfer and rise rate for clean and dirty bubbles in Clift et al. (1978). Bubbles are initialized with a clean interface and transition to a contaminated interface after a transition time that depends on the initial bubble size and the hydrate potential. The transition time was calibrated using the field experimental data in Rehder et al. (2009). From the model calibration, we found that the transition time depends on the initial bubble size and can be accelerated by hydrate formation. We validated the model using data from biogenic seeps in Römer et al. (2013), and further applied the hydrate formation prediction in an integral plume model to quantify dissolution for the Deepwater Horizon. The result shows that hydrate shells on bubbles form rapidly at deep sites, but go not inhibit mass transfer below standard values for contaminated interfaces.

Experimental Investigation on Methane Bubble Rise Velocities - The Relevant Influencing Parameter under Deep-sea and Ambient Conditions

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Due to the high gas to oil ratio at the deep-sea blowout of the Deepwater Horizon, the hydrodynamics of the plume was mainly dominated by the buoyancy and rise velocity of methane bubbles. Despite the fact that the distribution of oil in the near- and far-field is initiated by buoyancy driven bubbly flow, there is little known about the rising behavior of methane bubbles in a deep-sea environment especially if methane hydrate is formed and covers the gas-liquid interface. To solve this problem a pressure laboratory has been established at Hamburg University of Technology to enable detailed investigations on free rising methane bubbles under artificial deep-sea conditions. At pressures of up to 150 bars and temperatures of down to 4 °C, the rising behavior of methane bubbles is mainly influenced by contaminants in artificial seawater as well as methane hydrate that covers the bubble interface. It will be shown that common equations are well suitable to predict the rise velocity of methane bubbles under artificial deep-sea conditions as long as the influence of contaminations and methane hydrate formation is taken into account. The equations for a reliable prediction of the buoyancy driven bubbly flow will be presented as well as the consequences for the near- and far-field modeling. By taking into account the buoyancy driven bubbly flow, the evolution of a future oil spill caused by a deep-sea

blowout, will be predictable much more accurate and reliable. This project was financed by BP/The Gulf of Mexico Research Initiative.

Bubble Characteristics at Two Gulf of Mexico Natural Gas Seepage Sites

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To understand the fate and transport of hydrocarbons released from the deep ocean, a field expedition (GISR Cruise G07) was carried out to collect data below the hydrate stability zone from two natural gas seep sites in the Gulf of Mexico (MC 118 and GC 600). Here, we present measurements of bubble composition, dissolved-phase gas concentration at the release point, and bubble characteristics using task-specific instruments mounted on an ROV. Gas bubbles were collected using isobaric gas-tight samplers (Seewald et al., 2002) and dissolved fluid was collected using a precision sampling system, the SUPR system (Breier et al., 2014). A stereoscopic, high-speed imaging system collected physical properties of the bubbles. A line of relatively clean gas bubbles were observed from the seep at MC 118, and more strongly oiled bubbles of larger size were observed at GC 600. Both sites had similar gas composition of about 90% methane by mole fraction. Gas concentration in the end-member fluid exiting the seeps was near saturation. High-speed imagery revealed a rigid bubble-water interface indicative of a hydrate skin for all measurements at MC 118 and for all bubbles more than 2 m above the sea floor at GC 600. Measurements at GC 600 closer to the source showed a fluid bubble-water interface, suggesting a hydrate formation time on the order of a few seconds. Bubble size distributions were between 1 to 10 mm in equivalent spherical diameter and in situ seep flow rates between 0.3 to 0.8 l/min at each site. Bubble characteristics were observed at 10, 20, 50, and 100 m above the sea floor. Images show the effects of size sorting by the crossflow.

Experimental Investigation of Droplet and Bubble Size Distribution in Single and Multiphase Oil/Gas Jets under Deep-sea Conditions

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The exploration of oil and gas at large drilling depths entails the risk of deep sea blowouts, as we learned from the Deepwater Horizon oil spill in the Gulf of Mexico 2010. The hydrodynamics of a gas-liquid blowout is complex because the interaction between seawater, gas bubbles and oil droplets depends on its buoyancy, shape and several other parameters. To predict the distribution of hydrocarbons and the evolution of a spill with near- and far-field models, reliable information about the gas bubble and oil droplet behavior is indispensable. The rising behavior and flow structure within the multiphase jet of a blowout depends on the bubble size distribution (BSD) and droplet size distribution (DSD) that is dominated by shear forces and particle properties. The higher the shear stress the more the bubble and droplet size distribution (BSD/DSD) is shifted to smaller bubbles and droplets. The solidification of the bubble interface by contaminations and hydrates counteracts the acceleration by buoyancy. Experimental results under high pressure/low temperature conditions will be presented for the prediction of BSD and DSD in single and multiphase jets. The influence of the flow regime, defined by

volume flow rates and orifice diameter, as well as the GOR will be discussed to enable an estimation of the impact of future blowouts.

Oil Droplet Dispersion Behaviour during Deepwater Blowout Conditions

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The uncontrolled release from deepwater hydrocarbon reservoirs will result in the dispersion of oil and gas into the water column. The physical and chemical properties of dispersed hydrocarbons govern their vertical and lateral migration through the deep ocean, and directly informs the necessary mitigation and remediation steps. Limited observations and data are available to describe the oil-in-water droplet size distribution across various blowout conditions, decreasing the accuracy of forecasts. In this study, we deploy a high-pressure sapphire cell, capable of dispersing crude oil in water; the transparent material enables direct visual observation of the oil. The cylindrical mixing geometry is a rigorously-studied shear environment, allowing us to directly evaluate the relationship between oil droplet size and the cell turbulence via the Reynolds number. We have constructed droplet size distributions over a range of turbulence conditions, crude oil type, water salinity (0 to 3.5 wt%), pressure (1 to 110 bar), and the amount of dispersant added to the system (0.1 to 2 wt% with respect to oil). The data have been utilized to generate a predictive model that captures both mean droplet size and distribution type, across the parameter ranges identified above. The results demonstrate arithmetic mean droplet diameters ranging from 100-400 microns under the turbulence conditions studied. This particle size distribution is similar to results that have been obtained in a free jet under deep-sea conditions. The predictive model was used to estimate droplet sizes produced in the Deepwater Horizon blowout in 2010, and the evolution of these droplets was studied using numerically rigorous far field simulations.

Session 018
Frontiers in Dispersant Science and Technology: From Molecular Mechanisms to Design of Novel Dispersants and Field Applications

New Dispersant Gel Treats Marine Oil Spills More Effectively with Less Product

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Applying chemical dispersants to offshore oil spills is often the best response to minimize environmental effects. ExxonMobil is developing a new dispersant with a gel-like consistency that enhances the performance of dispersants as a response option for marine spills. Wave-basin tests found that the new dispersant's increased viscosity and greater active ingredient content allowed dispersion of conventional oils with dispersant-to-oil ratios as low as 1:60 or lower (compared to 1:20 typically used for dispersants) and dispersion of oils currently considered too viscous, e.g., heavy crude oils, fuel oils, or oils that become viscous in Arctic climates. The new formulation treated heavy crude and fuel oil significantly better than a widely available dispersant in side-by-side tests. Further, the new formula worked better in cold temperatures. The new dispersant may more than triple the treatment capacity of a single plane

load of dispersant, and disperse oils currently considered undispersable because of naturally high viscosity, weathering, emulsification, or cold temperatures.

Informing the Design of New Oil Dispersants through Studies of Dispersant-Oil Mixtures' Dynamic Interfacial Tension and Microstructure

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A “model crude oil” containing nonpolar aliphatic and aromatic compounds in proportions similar to those found in Macondo crude oil has been developed to facilitate the study of microstructures formed by dispersants in marine crude oil slicks. Initial and dynamic interfacial tensions exhibited by various mixtures of Tween 80, Span 80, and dioctyl sodium sulfosuccinate (DOSS) in the model oil are similar to those observed when the same surfactant mixtures are added to crude oil, including (and most notably) at those mixture compositions which produce ultralow (<10^-3 mN/m) interfacial tensions and high oil dispersion effectiveness. At overall surfactant concentrations of 2 wt% (~25 mM), typical for dispersant-treated oil and greater than concentrations at which reverse micelles have previously been reported for DOSS (~1 mM) and for Tween 80/Span 80 mixtures (~20 mM) in nonpolar solvents, water-in-oil microstructures have been observed and characterized for various Tween 80/Span 80/DOSS mixtures. Such microstructures likely play a key role in solubilizing hydrophilic components of dispersants, such as Tween 80, into dispersant-treated oil slicks, and point to the importance of incorporating surfactants which readily form reverse micelles, such as DOSS, into dispersants. Based on this insight, a new dispersant has been formulated which contains soy lecithin, a natural amphiphile known to form water-in-oil microstructures, among other food-grade surfactants, and which performs comparably to Corexit 9500 in the Baffled Flask effectiveness test.

Multifunctional Microgel Dispersions for the Absorption and Release of Surfactant Dioctyl Sodium Sulfosuccinate (DOSS)

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Solid particles may serve as effective potential dispersants in oil drilling and recovery. We investigate the design and synthesis of multifunctional microgel dispersions with a tunable range of behaviors in which the particles undergo extensive reversible volume phase transitions in response to environmental stimuli such as temperature and pH. Owing to their unique environmental sensitivities the prepared particles can potentially be applied towards novel interfacial engineering by equilibrating at oil-water interfaces, subsequently varying the interfacial tension between the salt water and crude oil phases, and selectively uptaking or releasing active species, such as synthetic oil dispersants dioctyl sodium sulfosuccinate (DOSS) surfactant contained in Corexit 9500A. This versatile approach may offer an innovative method to engineer oil-water interfaces for oil spill remediation and recovery.

Magnetite Nanoparticles Stabilized by Halloysite Clay Nanotubes for Oil Emulsification and Electromagnetic Remote Sensing

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The interfacial-activity of naturally-occurring halloysite clay nanotubes (HNT) has been synergized with the magnetic properties of magnetite nanoparticles (Fe3O4) for potential applications in the dispersion, enhanced bioremediation and electromagnetic remote sensing of oil spills. The dispersion of surface oil layers on water into tiny droplets represents an effective response mechanism in the treatment of oil spills. This can increase oxygen transport from the atmosphere to the water, enhance oil biodegradation by the native microbial population and reduce the possibility of shoreline impact. Monitoring the fate and transport of dispersed oil is also an important aspect of the oil spill remediation process. The HNT-stabilized magnetite nanoparticles (MAGHNT) were prepared using a simple in-situ co-precipitation method. The MAGHNT is effective in stabilizing oil-in-water emulsions and are superparamagnetic making it attractive as a contrast agent for the electromagnetic sensing of oil spills. The hollow nanotubluar morphology of the MAGHNT offers an opportunity for the loading and delivery of surfactants to the oil-water interface. The lumen volume of MAGHNT was loaded with the anionic surfactant, dioctyl sulfosuccinate sodium salt (DOSS) and the non-ionic surfactant, polyoxyethylene (20) sorbitan monooleate (Tween 80). The synergistic adsorption of MAGHNT and the released surfactants effectively stabilizes the emulsions. The simple synthesis procedure and use of a naturally occurring aluminosilicate clay nanotube makes this multifunctional material attractive for several aspects of the oil spill remediation process.

Simulations of Tween® 80 Monolayers and Micelles: Structure and Adsorption Energetics

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Tween® 80 (Polyoxyethylene sorbitan oleate) is a main component in Corexit® oil dispersant. To study microscopic structure and interfacial tension (IFT) reduction, we build an atomistic model for Tween® 80 simulation. In a preassembled micelle with 60 molecules, the radial distributions of tail and headgroup are found to be insensitive to stereo-isomerization, but sensitive to changes in relative lengths of the four poly(ethylene oxide) (PEO) chains in the headgroup. At the air-water and oil-water interfaces, the IFT is significantly lower for the constitutional isomer with the shortest PEO chain bridging the tail and the sorbitan ring. The IFT for Tween® 80 isomers with multiple tails is also significantly lower. The results indicate possible scope for enhancing IFT reduction of Tween® 80. We also inspect the energetics of Tween® 80 adsorption. After validating the forcefield for PEO adsorption energetics, we measure free energy profiles (FEPs) of PEO oligomers, oleic acid, and a model Tween® 80 molecule at water/alkane interfaces. We decompose the adsorption free energy of Tween® 80 at a neat water/alkane interface into contributions: 1) desorption of PEO chains from interface, 2) transfer of tail from interface to water, 3) shielding of tail by headgroup. Based on the FEPs, we found the model Tween® 80 molecule adsorbs irreversibly at dilute interfaces, with a crossover to kinetically-limited desorption at higher surface concentration, in agreement with experiments by Reichert and Walker [Langmuir 29, 6 (2013)]. Time permitting, we describe efforts to understand how surfactant crowding affects adsorption energetics.

Overcoming the Critical Micelle Concentration: Exploring Nanoparticles with Amphiphilic Grafts as Concentration-independent Unimolecular Micelles

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Small molecular surfactants, such as Corexit, form micelles around droplets of oil to disperse the hydrocarbons in bulk water. However, all small molecule surfactants exhibit an inherent critical micelle concentration and therefore disaggregate when diluted in large bodies of water. Nanoparticles with amphiphilic polymer grafts, on the other hand, can exhibit a hydrophilic corona to provide dispersibility in water and a lipophilic inner block that provides a domain for oil encapsulation, yet the nanoparticle core itself provides a scaffold that prevents disaggregation even under extreme dilution.These amphiphilic grafted nanoparticles (AGNs) were prepared in a cost-efficient manner by 1) surface hydroxylation of silica nanoparticles, 2) caprolactone polymerization and 3) poly(ethylene glycol) (PEG) coupling. The three materials selected: silica, polycaprolactone (PCL), and PEG were chosen because they are all highly biocompatible. Also, due to the modular nature of the design, the size of each of these components can be tailored to optimize hydrocarbon encapsulation. Physical measurements confirm that the AGNs are water-suspendible, exhibit true unimolecular micelle-behavior, and rapidly encapsulate hydrocarbons. Furthermore, quantification studies reveal that controlling the size of the PCL block enables the encapsulation capacity of the AGNs to be increased. Ongoing investigations seek to tune each of the design parameters to optimize AGN performance as a dispersant.

Phase Behavior of Dilute Carbon Black Suspensions and Carbon Black Stabilized Emulsions

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We use functionalized carbon black (CB) as a model particulate material to study the effect of salt-modulated attractive interactions on phase behavior and steady shear stresses in suspensions and particle-stabilized emulsions. We tune attractive interactions by adding NaCl to the suspension, thus salting surface carboxylate groups and leading to hydrophobic interactions in addition to van der Waals attractive potentials. Yield stress behavior emerged at a volume fraction of CB as low as $\varphi CB = 0.008$. Yield stress scaled with CB concentration with power law behavior, which changed abruptly at a critical CB concentration to a much larger power, suggesting a substantial change in network structure. Electron microscopy imaging revealed structural differences between the networks found in each scaling regime. Randomly oriented pores within thick CB boundaries were observed in the higher power scaling region, suggesting a strong gel network, and long, oriented pores were found in the lower power scaling region, suggesting influence by the weight of the sample. These findings correlate with the existence and boundary between gels and transient networks, where the gel regime can be attained through increased particle concentration or increased attractive interaction potential. The yield stresses of CB- gels containing oil emulsion droplets were found to scale similarly with carbon black concentrations, implying that CB networks can be applied to capture, stabilize and contain discrete oil droplets within a rigid structure. These results offer insight into salt-induced attractive colloidal networks and the difference in structure between transient networks and gels.

Molecular Interaction of Different Surfactants with Oil at the Air-Water Interface

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Dispersant use can be considered as one of the most effective ways to combat off-shore oil spills. Nevertheless, there is still debate regarding the innocuity of current dispersant (Corexit) use and its transport into different environmental sections including air, water, sediment, and biota. Dispersants consist of a mixture of solvents and surfactants. In this study, we examined the extent of the effect of surfactants on the aerosolization of oil/dispersant matter into the atmosphere by bursting bubbles. These bursting bubbles are produced by an annular shear sparger in a laboratory aerosolization reactor. Over the course of experiments, the same molar concentration of each surfactant (Span80-Tween 80-Tween 85-DOSS) in oil was injected into the reactor individually. When reactor reaches to steady state, its effluent, including both vapors and particles, was collected and analyzed by GC-MS and LC-MS-MS. Our results show that different surfactants with different HLB and structures have various effects in ejection of organic matter into the atmosphere and also the dispersion of oil inside the reactor. For instance, we can see a significant difference between DOSS and Span 80 in their effect on the adsorption of organic matter to the surface of bursting bubble and their consequent ejection into the atmosphere. These observations can help us to have a better understanding about the oil and surfactant interaction at the air-water interface and to implement possible corrections to the current dispersant formulation.

Characterization of the Interfacial Behavior of a Model Dispersant-Biosurfactant System

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Corexit® and other dispersants used in oil spill remediation are comprised of multiple surfactants. Natural biosurfactants produced by oil-metabolizing bacteria are also present in the marine environment. Understanding the interaction of these multi-component systems at oil/water interfaces is crucial for improving dispersant design and application efficacy. Tween 80, a major component of Corexit®, has been shown to irreversibly adsorb to oil/water interfaces. Using a microtensiometer, we generate interfaces that have been coated with different initial amounts of Tween 80. We measure an effective isotherm of the irreversibly adsorbed component of Tween 80 and estimate its interfacial coverage. These Tween-coated interfaces are then exposed to bulk solutions of either Aerosol-OT, another significant Corexit® component, or rhamnolipid biosurfactant. We observe additional surfactant adsorption to the interface as a function of concentration, and interpret the resulting interfacial tension values using a Langmuir isotherm model. Tween 80 inhibits the secondary adsorption and remains largely irreversibly adsorbed even after exposure to high concentrations of AOT and rhamnolipid. These results have important implications for the mechanisms by which dispersant mixtures function in oil spill remediation.

Investigating the Effects of Critical Structural Parameters on the Loading Capabilities of Amphiphilic Grafted Nanoparticles: Characterization and Design Optimization

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In order to overcome potential ecological effects and limited efficiency due to emulsion instability of the traditional dispersants, amphiphilic grafted nanoparticles (AGNs) were prepared in a cost-efficient manner, using biocompatible materials, by a combination of surface hydroxylation of silica nanoparticles, caprolactone polymerization, and poly(ethylene glycol) coupling. The efficiency of these macromolecular materials in encapsulating oils was investigated by light scattering (LS)-based unique methodologies together with traditional methods. The first series of experiments designed to monitor stability and dynamics of the nanoparticles in aqueous media confirmed that AGNs are water-suspendible due to their hydrophilic corona, exhibit unimolecular micelle-behavior since nanoparticle core provides a scaffold to prevent disaggregation under dilution, and encapsulate hydrocarbons since polycaprolactone (PCL) inner block provides a domain for oil sequestration. It was also found that ionic strength does not impact significantly particle stability. Since these hybrid nanomaterials were designed for application as sequestering agents, next experiments investigated their loading capabilities using Gulf of Mexico crude oil from NIST and other organic molecules. The characterization studies focused on understanding of how critical structural parameters, such as hydrophilic/hydrophobic block ratio, affect their performance. UV and LS experiments indicated that increasing the amount of grafted PCL boosts the encapsulation; however, further increase leads to more complex behavior. Ongoing study focuses on investigating selective affinity in time toward aromatic vs. aliphatic components of the oil.

The Response of Surfactant Stabilized Oil-in Water Emulsions to the Addition of Particles in an Aqueous Suspension

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As a model for understanding how dispersant-stabilized emulsions respond to the addition of interacting and non-interacting particles that may be present in the ocean, we investigated the response of dodecane-in-water emulsions stabilized by SDS(anionic), CTAB(cationic) and Triton X-100(non-ionic) surfactants to the addition of an aqueous suspension of negatively charged fumed silica particles. The stability of the emulsion droplets and the concentration of surfactants/particles at the oil-water interfaces are sensitive to surfactant-particle interactions, mixing conditions and the particle concentration in the bulk. Addition of the particle suspension to the SDS-stabilized emulsions showed no effect on emulsion stability. The emulsion droplets coalesce when fumed silica particles were added to emulsions stabilized by Triton X-100. Depending on the concentration of silica particles in the suspension, the addition of fumed silica particles to CTAB-stabilized emulsions resulted in droplet coalescence and phase separation of oil and water, or formation of particle-coated droplets. Vigorous (vortex) mixing allows the particles to breach the oil-water interfaces, and the particles help stabilize emulsions. While we have examined a specific particle suspension and a set of three surfactants, these observations can be generalized for other surfactant-particle mixtures.

Session 019
Predicting the Ocean Environment

Impact of Glider Data Assimilation on the Predictability of the Meso-scale Circulation in the Gulf of Mexico

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We examined the impact of glider observations of temperature (T) and salinity (S) on the predictability of meso-scale circulation in the Gulf of Mexico (GoM) by producing ocean state estimates and forecasts. The state estimation used the Massachusetts Institute of Technology - general circulation model (MITgcm) and its adjoint-based strong constraint four-dimensional variational (S4DVAR) method to match the model evolution to observations by adjusting model T and S initial conditions, open boundary conditions, and atmospheric forcing fields. Assimilation experiments were conducted by fitting the model to satellite-derived along-track sea surface height (SSH), separated into temporal mean and anomalies, with and without glider (T and S) observations for multiple one month or two month segments from 2011 onwards. The optimized state from the end of the each assimilation period was used to initialize a forecast for two months using climatological forcing, open boundary conditions from assimilated 1/12 degree HYCOM climatology, and run-off fluxes. The hindcasts and forecasts from each experiment were compared with SSH data as well as to glider T and S observations. The model forecast for SSH and sub-surface ocean state was generally better than the persistence forecast (keeping the initial state fixed) and the control forecast (forecast initialized using assimilated HYCOM 1/12 degree global analysis) over periods longer than about 1 month. The inclusion of glider observations improved the long-term (two month) predictability for both SSH and sub-surface ocean state relative to the control forecast (from HYCOM). This contrasted with only short-term improvement (less than 1 week) of the SSH predictability compared to the control forecast using when only SSH was assimilated.

Data Assimilation Considerations for Improved Ocean Predictability during the Gulf of Mexico Grand Lagrangian Deployment (GLAD)

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Ocean prediction systems rely on an array of assumptions to optimize their data assimilation schemes. Many of these remain untested, especially at smaller scales, because sufficiently dense observations are

very rare. A set of 295 drifters deployed in July 2012 in the north-eastern Gulf of Mexico provides a unique opportunity to test these systems down to scales previously unobtainable. In this study, background error covariance assumptions in the 3DVar assimilation process are perturbed to understand the effect on the solution relative to the withheld dense drifter data. Results show that the amplitude of the background error covariance is an important factor as expected, and a proposed new formulation provides added skill. In addition, the background error covariance time correlation is important to allow satellite observations to affect the results over a period longer than one daily assimilation cycle. The results show the new background error covariance formulations provide more accurate placement of frontal positions, directions of currents and velocity magnitude. These conclusions have implications for the implementation of 3DVar systems as well as the analysis interval of 4DVar systems.

An Assessment of the Lagrangian Predictive Skill of a Navy Coastal Ocean Model Ensemble in the Northern Gulf of Mexico using GLAD Drifters

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In July 2012, more than 300 near-surface GPS tracked drifters were launched in the vicinity of the Deepwater Horizon site as part of the Grand Lagrangian Deployment (GLAD) experiment. These drifters were drogued at a depth of one meter and reported their positions in real-time at five-minute intervals as they moved through the northeastern Gulf of Mexico. Ensemble surface current forecasts from the Navy Coastal Ocean Model (NCOM) were later performed to study the synoptic surface circulation in the GLAD experiment area. The extensive set of high-resolution GLAD drifter tracks provides a unique opportunity to assess these ensemble forecasts. Here, the Lagrangian predictive skill of the NCOM ensemble is evaluated using more than 220 GLAD drifters during September 2012. The drifter tracks were divided into non-overlapping uniform three-day segments, with “launches” at three-day intervals, at midnight. This scheme produced more than 1000 trajectory segments. Observed trajectories over three days are compared with ensemble trajectory predictions and the statistics from a number of skill metrics are used to quantify the ensemble’s Lagrangian predictive skill.

Coupled Ocean-Air-Wave Predictions in the Gulf of Mexico

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The Coupled Ocean Air Mesoscale Prediction System (COAMPS) has been configured for the Gulf of Mexico and is running in real time. This configuration has a 3 km ocean model based in NCOM, a 2 km atmospheric model based on COAMPS (a triple nest from the global solution), and a 6 km wave model based on SWAN. This is a 5-way coupled system, i.e. atmosphere to ocean (and vice-versa), atmosphere to wave, and ocean to wave. This implementation uses the recently transitioned NAVGEMS (instead of NOGAPS) for boundary conditions. Many new features have been added to the code, such as the ability to separate the ocean and atmospheric data assimilation cycles (this system uses 12 hours and 24 hours, respectively), more friendly file formats for the wave output, and the ability to run the three components either sequentially or concurrently (this version runs concurrently). The current configuration cycles on the atmosphere every 12 hours and on the ocean every 24 hours. A 72 hour forecast for all components (air, ocean, wave) is generated once per day. The system ingests all available

ocean observations via NCODA and all available atmospheric observations via NAVDAS. There is currently no wave observation assimilation. The mesoscale features compare well to other systems running in the Gulf of Mexico, but the higher resolution atmospheric forcing results in more energetic flows, particularly in the littoral regions. The Stokes drift is included into the ocean via the wave forcing, and give more realistic forecasts of mixed layer depth in some regions. Comparisons with a non-coupled 3 km ocean system (that excludes wave forcing) are discussed.

Evaluation of Impact of DWH Rapid-response Surveys on Numerical Forecasts using Observing System Simulation Experiments

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The first rigorously evaluated prototype ocean Observing System Simulation Experiment (OSSE) system has been developed in the Gulf of Mexico, following the well-established methodology of atmospheric OSSEs. This OSSE system has been used to investigate the impact of assimilating rapid-response airborne ocean profiles deployed in response to the Deepwater Horizon oil spill in 2010. Nine surveys using the Hurricane Hunter NOAA WP-3D aircraft were undertaken, with the deployment of various profiling instruments in the Loop Current and neighboring areas. We considered this reference campaign to study alternative deployment scenarios, toward the optimization of future similar campaigns to achieve maximum effect on analysis and forecast skills. In particular, we calculated error and bias reduction in key ocean variables to quantify the impact of: a) the frequency of airborne surveys; b) spatial resolution of probe deployment along the aircraft pathway and c) various types of probes. Results show that for the airborne profiles to strongly constrain model upper-ocean dynamical and thermal fields, repeated surveys must be conducted at least every 4 days. Probes have to be deployed at a relatively high resolution (0.5 degree) in order to provide substantially larger impact compared to 1.0 degree. Measuring salinity along deep profiles using airborne CTDs provides additional constraint to upper-ocean dynamical fields compared to shallower XBT profiles. Our Gulf of Mexico OSSE system has been recently upgraded to high resolution (1/50 degree), high frequency boundary conditions and improved representation of coastal dynamics. Examples of high resolution system evaluation will be presented.

Sensitivity of Surface Tracers in the Gulf of Mexico using the Navy Coastal Ocean Model

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Statistics of Extremes in Oil Spill Risk Analysis

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The Deepwater Horizon oil spill (DWH) in 2010 in the Gulf of Mexico is the largest accidental marine oil spill in the history of the petroleum industry. After DWH, key questions were asked: What is the likelihood that a similar catastrophic oil spill (with volume over one million barrels) will happen again? Is DWH an extreme event or will it happen frequently in the future? The extreme value theory (EVT) has

been widely used in studying rare events, including damage from hurricanes, stock market crashes, insurance claims, flooding, and earthquakes. In this paper, the EVT is applied to analyze oil spills in the U.S. outer continental shelf (OCS). Incorporating the 49 years (1964-2012) of OCS oil spill data, the EVT is capable of describing the oil spills reasonably well. The return period of a catastrophic oil spill in OCS areas is estimated to be 165 years, with a 95% confidence interval between 41 years and more than 500 years. Sensitivity tests indicate that the EVT results are relatively stable. The results of this study are very useful for oil spill risk assessment, contingency planning, and environmental impact statements on oil exploration, development, and production.

The Influence of Grid Resolution and Wind Specification on the Prediction of Transport of Oil at the Surface

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Prediction of oil transport is fundamentally influenced by the hydrodynamic model which makes circulation predictions. We investigate the influence of hydrodynamic model grid resolution and wind specification on the prediction of surface oil transport using the Lagrangian TRANSport (LTRANS) model and three Regional Ocean Model System (ROMS) hydrodynamic models. Two of the hydrodynamic models are Gulf-wide and have grid resolutions of 5 km (SABGOM) and 3 km (CRCM). One is forced with winds from the North America Regional Reanalysis (SABGOM) while the other (CRCM) is fully coupled to an atmospheric model (WRF). In addition, a high resolution coastal model (TXLA) has 1 km grid spacing. All were applied in hindcast mode to simulate the Deepwater Horizon oil spill. Trajectories of oil at the surface were simulated within both Gulf-wide model domains, and from the Gulf-wide models into the coastal model domain. Results are compared between models and with observations of oil slick locations to identify how grid resolution and wind parameterization influence prediction of surface oil transport. Findings and challenges will be discussed.

Direct Sea Surface Height Data Assimilation in the Gulf of Mexico

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New methods are developed for assimilating satellite sea surface height anomaly (SSHA) and velocity observations into a numerical ocean model of the Gulf of Mexico. Vertical correlations, derived from historical ocean profiles of temperature (T) and salinity (S), are used to relate T and S to geopotential (G) by integrating the specific volume anomaly vertical structure. The resulting vertical correlations (of T & T, T & S, T & G, S & S, etc.) are then used to assimilate SSHA and velocity observations by creating increments of subsurface T, S, and velocity. Velocity is related to G using the geostrophic relation. Since satellite derived SSHA observations are the most important data stream used to improve numerical ocean forecasts, this presentation will focus on SSHA data assimilation. The Naval Research Laboratory traditionally employs a method where SSHA data is used to create ocean synthetic subsurface profiles of T and S, which are then assimilated as observations in an ocean forecasting system. The latest version has a one-dimensional variational scheme based on historically observed ocean vertical correlations for T and S globally at ½ degree resolution. The new method uses these correlations directly within the 3DVAR Navy Coupled Ocean Data Assimilation system, without making synthetics. The results from both

assimilation methods will be compared and discussed. The currents and current directions from these assimilation methods are validated relative to the 295 drifters deployed in July 2012 in the north-eastern Gulf of Mexico as part of the Gulf of Mexico Grand Lagrangian Deployment (GLAD).

Do Assimilated Drifter Velocities Improve Lagrangian Predictability in an Operational Ocean Model?

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The Lagrangian predictability of general circulation models is limited by the need for high-resolution data streams to constrain small-scale dynamical features. Here velocity observations from Lagrangian drifters deployed in the Gulf of Mexico during the summer 2012 Grand Lagrangian Deployment (GLAD) experiment are assimilated into the Naval Coastal Ocean Model (NCOM) 4D variational (4DVAR) analysis system to examine their impact on Lagrangian predictability. NCOM-4DVAR is a weak-constraint assimilation system using the in-direct representer method. Velocities derived from drifter trajectories, as well as satellite and in-situ observations are assimilated. Lagrangian forecast skill is assessed using separation distance and angular differences between simulated and observed trajectory positions. Results show that assimilating drifter velocities substantially improves the model forecast shape and position of a Loop Current ring. These gains in mesoscale Eulerian forecast skill also improve Lagrangian forecasts, reducing the growth rate of separation distances between observed and simulated drifters by approximately 7.3 km day-1 on average, when compared with forecasts that assimilate only temperature and salinity observations. Trajectory angular differences are also reduced.

Variational Data Assimilation and Sensitivity of Surface Tracers Using the Navy Coastal Ocean in the Gulf of Mexico

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Identification of the source of pollutants or debris on the surface of the ocean depends on an accurate knowledge of the ocean circulation, which requires that an ocean circulation model be combined with available ocean observations in a data assimilation process. The resulting ocean analysis can then be used for sensitivity studies in which surface tracers are advected either forward or backward in time to determine where the tracer will end up or where it came from. Because the velocity field advecting the tracer needs to be known accurately, the data assimilation process should not be short-circuited or by-passed, as it could lead to erroneous conclusions and decisions. An example of the assimilation and sensitivity processes will be shown for the Gulf of Mexico.