Poster Presentations

Session 001: Data Management and Informatics Supporting Ecosystem Sciences

Sufficiency of Self-Documenting Data Exchange Standards

F. Gayanilo[1], M. Howard[2]
[1]Texas A&M University-Corpus Christi, Corpus Christi, TX, [2]Texas A&M University, College Station, TX

Scientific data warehouses continue to proliferate with a common goal of securing and distributing the data at some future time for reuse or reanalysis. Establishing data provenance is a major concern of data centers, realizing that failures to establish data provenance inhibits the reuse of the data and voids the effort to archive the data. The International Organization for Standardization (ISO), an international standardization organization, has published metadata standards, such as the ISO 19115-2, that are widely popular and designed to establish data provenance. There are other standards development groups like the Open Geospatial Consortium (OGC) that are also publishing similar standards. Ocean observing communities, specifically, members of the Integrated Ocean Observing System (IOOS) Association are adopting the OGC Sensor Observation Service (SOS) and Sensor Web Enablement (SWE) to promote interoperability among similar systems. The data served by these web services defines what data is collected, period it was collected, how it is collected and who are responsible for the data. This paper discusses the application of the SOS and SWE as community standards and evaluates sufficiency of the attached information to give users confidence needed to reuse the sensor data extracted.

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

Dispersant Effectiveness of Corexit 9500A for Fresh/Weathered Crude Oil and for Some Aliphatic/Aromatic Compounds of Crude

D. Boglaienko, B. Tansel
Florida International University, Miami, FL

Crude oil consists of saturates (around 80%) and aromatics (around 13%), and the rest is resins, asphaltenes and waxes (South Louisiana Crude oil, SLC). The most toxic components belong to aromatics: mononuclear (MAH) and polynuclear aromatic hydrocarbons (PAH). As part of the weathering process, MAH evaporate first. A dispersant, applied immediately after a spill, would cause more aromatics to be dissolved. The objective was to analyze dispersant effectiveness (DE) of Corexit 9500A for weathered (WO) and nonweathered crude oil (NWO). Oil was weathered in a hood during 2 months at the room temperature. Additionally, DE experiments for saturates and aromatics were performed. Three mixtures were designed: Alkanes (C10, C14, C16); MAH (benzene, toluene, and ethylbenzene); Alkanes and MAH. All mixtures were dyed with Sudan IV red dye. The series of experiments were conducted for salt water (34 g/L); dispersant to oil ratio 1:20; at room temperature, and 200 rpm rotation speed. DE analysis was performed similar to the oil extraction with dichloromethane, EPA Swirling Flask Test (US EPA, 1996). Concentrations of dispersed organic compounds were analyzed using UV-visible spectrophotometer. Statistical test ANOVA was conducted to evaluate differences between DE of the hydrocarbon mixtures. Paired-samples t-test was utilized to

compare differences in DE of WO and NWO. Results revealed that DE of Alkanes is significantly higher (p = 0.000) than DE of any other group. DE of NWO is significantly higher than DE of WO (p = 0.03).

Spatial Distribution of Natural Radionuclides in Soil, Sediment and Waters in Oil Spilled Areas in Niger Delta Region of Nigeria

A. O. N. Ezekiel[1], A. G. Gregory[2]
[1]Federal University of Petroleum Resource, Effurun, Nigera, Ughelii, Nigeria, [2]University of Port Harcourt, Rivers State, Nigeria, Port Harcourt, Nigeria

Activity concentrations of natural radionuclides (226Ra, 232Th and 40K) in the soil, sediment and water of oil producing communities in Delta and Rivers States were determined using γ-ray spectrometry. The mean soil/sediment activity concentration of 226Ra, 232Th and 40K in onshore west in Delta state is 40.2±5.1 Bqkg-1, 29.9±4.2 Bqkg-1 and 361.5±20.0 Bqkg-1 respectively, the corresponding values obtained in onshore east1 of Rivers state is 20.9±2.8 Bqkg-1, 19.4±2.5 Bqkg-1and 260.0±14.1 Bqkg-1 respectively. While the mean activity concentration of 226Ra, 232Th and 40K in onshore east2 of Rivers state is 29.3±3.5 Bqkg-1, 21.6±2.6Bqkg-1 and 262.1±14.6Bqkg-1 respectively. These values obtained show enhanced NORMs but are well within the world range. All the radiation hazard indices examined in soil have mean values lower than their maximum permissible limits. In the water samples collected, the values obtained are well above world average values of 1.0, 0.1 and 10 Bql-1 for 226Ra, 228Ra and 40K respectively, those of the control site values and most reported values around the world. Though the hazard indices (Raeq, Hex, Hin) examined in water is still within tolerable level, the committed effective dose estimated are above ICPR 0.1 mSvy-1 permissible limits. The overall results show that soil and sediment in the area are safe radiologically but the result indicates some level of water pollution in the studied area.

High Resolution Seafloor Data to Guide Sampling and Data Interpretation

A. Diercks[1], V. Asper[2], R. Jarnagin[1], M. Woolsey[1], M. D'Emidio[3], S. Tidwell[3], A. Conti[4]
[1]University of Southern Mississippi, Abbeville, MS, [2]University of Southern Mississippi, Stennis Space Center, MS, [3]University of Mississippi, University, MS, [4]University of Mississippi, University, MS

Deep-sea seafloor surveys obtained by autonomous underwater vehicles provide the very high resolution spatial data needed to interpret seafloor and in some cases water column phenomena and processes. In the first two years of the ECOGIG program funded by GOMRI, two deep sea AUV's provided seafloor morphology, sub-bottom structure and photo mosaics, of three areas chosen by the ECOGIG consortium as their main study sites. During a cruise this summer, site OC26 about 3 nm to the SSE of the Macondo wellhead, was revisited by the AUV group with their photographic AUV to investigate specific bottom structures found during a previous multibeam echo sounder survey of the area. Detailed image data from these dives show not only active mud-volcanoes but also hydrate outcrops unknown at this site. Findings like these make it very clear that to understand seafloor and water column processes, spatial and temporal high resolution data of morphology, sub bottom structures and photomosaic surveys are needed to properly describe the environment and make decisions about sampling sites and methods. Without high resolution data we could potentially miss some of the sources of the materials we find contributing to the specific questions we try to answer using sediment traps and benthic landers.

Oil-Dispersant-Sediment Interactions and Effects of Dispersant on Sorption/Desorption of PAHs with Gulf Coast Marine Sediments

X. Zhao
Auburn University, Auburn, AL

This presentation provides a state-of-the-science overview on the oil, dispersant and sediment interactions, and presents related experimental findings on effects of oil dispersants on sediment sorption/desorption of four model PAHs (naphthalene, 1-methylnaphthalene, phenanthrene and pyrene). The review summarizes the state of science pertaining to effects of oil dispersants on sediment sorption/desorption and availabilities of oil components, and discusses their roles in oil distribution between water column and sediment particles. Effects of sediment properties, dispersant type, waster salinity and pressure on oil-sediment interactions are also addressed. Experimental data on effects of a model oil dispersant (Corexit EC9500A) on sorption/desorption of four PAHs with two marine sediments are presented. Kinetic tests and sorption isotherms revealed that the dispersant poses two opposing effects: it enhances the sediment sorption of PAHs through adsolubilization, but may also facilitate dispersion of PAHs in water, and the net effect will depend on sediment type, PAH hydrophobicity, and dispersant concentrations. For example, the dispersant at low concentrations (18 mg/L) enhanced the uptake of all four PAHs, but inhibited pyrene uptake at elevated dispersant concentrations. The presence of the dispersant during desorption induced remarkable hysteresis; and elevated PAHs uptakes were observed at deepwater conditions (4 °C and 16 MPa).

Effect of Chain Length and Grafting Density on Oil Uptake in Amphiphilic Copolymer Grafted Silica Nanoparticle Systems

K. C. Bentz[1], S. E. Walley[1], N. M. Vogelpohl[2], N. V. Bhikha[3], D. A. Savin[1]
[1]University of Southern Mississippi, Hattiesburg, MS, [2]University of California, Santa Barbara, Santa Barbara, CA, [3]University of Mississippi, Oxford, MS

Silica nanoparticles (SNPs) have been grafted with amphiphilic copolymer polycaprolactone-b-polyethylene glycol (PCL-b-PEG) using both grafting-from and grafting-to techniques. Surface bound hydroxyl initiating species were introduced to the SNPs via immobilization of 3-glycidoxypropyldimethylethoxy silane (GPDMES) and subsequent ring opening of the epoxide functionality, from which ε-caprolactone was polymerized. Additionally, initiating groups were spaced on the SNP surface by immobilization of trimethylethoxy silane (TMES), which cannot initiate polymerization, at various ratios with GPDMES. Finally, PEG was grafted to the surface of the SNP-PCL by esterification of acid functionalized PEG with the native hydroxyl end group on the PCL chain. Grafting of PEG yields particles that are dispersible in water, and capable of taking up hydrophobic material. Polymerization of ε-caprolactone from surfaces with higher densities of initiating species results in more grafted polymer per mass of SNP at equivalent reaction times than for lower densities of initiating groups, as measured by weight loss in thermogravimetric analysis. Interestingly, there is little correlation in brush length measured by dynamic light scattering for polymer grafted SNPs at various grafting densities due to factors such as chain constraint and molecular weight of grafted chains. It is investigated herein how factors such as grafting density, hydrophobic and hydrophilic chain lengths, and environmental conditions such as water temperature and salinity affect oil uptake for these materials.

Synthesis of Cactus Based-Mucilage Dispersant and Titanium Dioxide Hybrid and its Application on Surface Tension of Oil/Water Emulsions

W. Zhao[1], S. Mesa[2], F. Guo[1], N. Alcantar[1]
[1]University of South Florida, TAMPA, FL, [2]The City College of New York, New York, NY

Cactus based-mucilage dispersant has been developed and tested to have the ability to reduce the average oil droplet size. Also, mucilage can disperse oil in oil/water emulsions by lowing the surface tension. Furthermore, mucilage has been proven to have a relatively low toxicity to marine organisms even at high concentrations. In all, cactus based-mucilage has very high potential to act as a biological dispersant. However, there are still some limitations for the use of dispersant especially for the weathered oil. It has persistent hydrocarbon fractions, which makes it harder to biodegrade by microorganisms. Photocatalytic treatment is an important process to increase the solubility of resistant hydrocarbons and the rate of subsequent biodegradation. In this research, titanium dioxide is used as a photocatalyst due to its high efficiency and low toxicity. As a preliminary research, two methods are applied to synthesis mucilage-TiO2 hybrid. Non-gelling extraction mucilage (NE) is used as dispersant compound. P25 and titanium isopropoxide are employed as the source of titanium dioxide. Microscopy pictures are taken to understand the surface morphology of hybrid. Surface tension tests are done to see if the hybrid can reduce surface tension of oil/water emulsions. As a result, with titanium to NE ratio of 1:10, the surface tension of oil/water emulsion can reduce from 44.98 (±1.33%) to 31.23 (±0.16%) when the dispersant to oil ratio is 6% (v/v). This result opens a path to explore a better mucilage-titanium hybrid synthesis method. This hybrid will extend the application of dispersant especially in weathered oil.

Session 003: Microbial Ecosystem Trajectories in Gulf of Mexico Environments

Alternative Bacteria Removal Method in Polluted Water Via Cactus Mucilage

T. Peng, F. Guo, D. Stebbins, R. Toomey, N. Alcantar
University of South Florida, Tampa, FL

The purpose of this research is to investigate an alternative treatment to remove bacteria from water using a natural biomaterial that can be used by communities in need--Mucilage. The mucilage that we are using is from *Opuntia ficus-indica* specie, commonly known as Nopal or Prickly pear cactus. The Nopal cactus pads are readily available, inexpensive and have been used to clean water by ancient communities in Mexico. Extensive research in our group has shown that the mucilage is efficient at removing turbidity, bacteria (*E. coli* and *Bacillus sp*.) and arsenic from contaminated water. We also are investigating the conditions under which cactus mucilage will be able to reduce the levels of a surrogate for *Vibrio Cholerae*, named *Vibrio furnissii*. Lyophilized pellets of the surrogate bacteria were purchased from a testing laboratory specialized in environmental and public health threats. Although the higher concentration of the mucilage (10 mg/L) did not decrease the bacteria concentration, the lower concentration of the mucilage (1 mg/L) removed 25% of the original concentration of the bacteria on the top of the water column. The treatment using 1 mg/L of mucilage plus calcium carbonate was determined to remove 40% of the bacteria. These preliminary studies suggest that mucilage from the *Opuntia ficus-indica* is a viable flocculation method for Cholera. Its low cost, accessibility, and current

use as a food source in low income communities give mucilage great potential as a water treatment method for areas such as Haiti that have had devastating bacterial contaminations.

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

Hindcast Modelling for the Persistence of Floating Oil Released from Natural Seeps

S. Daneshgar Asl, D. S. Dukhovskoy, M. Bourassa, I. R. MacDonald
Florida State University, Tallahassee, FL

The GC600 natural hydrocarbon seep site, situated on a low-relief ridge at a depth of about 1250 m is a perennial source of surface oil slicks in the Gulf of Mexico. The primary objective of this work is to estimate the surface residence time of those oil slicks using an ocean current model. Included in the ocean model is a random-walk parameterization of oil turbulent diffusion. A Texture Classifying Neural Network Algorithm (TCNNA) was used to delineate oil slicks in satellite SAR images. The oil slicks from the GC600 region were detected clearly 46 times in images collected from January 2004 to November 2011. The ocean surface currents were obtained from the HYCOM (Hybrid Coordinate Ocean Model) Gulf of Mexico 1/25-degree analysis and the wind history data during the days before SAR imaging were obtained from CCMP (Cross-Calibrated Multi-Platform) data base. Previous comparisons between the geometrical shape of the slick from the TCNNA outline to that predicted by wind only indicated an average oil surface residence time of approximately 12 hours; however, the ocean currents significantly modify this result.

Oil Spill Risk Assessment of Singapore Strait Based on 3D Lagrangian Multiphase Oil Spill Modelling

K. Gong[1], P. Tkalich[1], H. Choo[1], V. Maderich[2], I. Brovchenko[2], G. Barbastathis[3]
[1]National University of Singapore, Singapore, Singapore, [2]Institute of Mathematical Machine and Systems, Kiev, Ukraine, [3]Massachusetts Institute of Technology, Cambridge, MA

The transport and fate of oil spilled in the sea are governed by the advection due to currents, spreading of the surface slick, mass transfer, changes in physicochemical properties and interaction of oil with the suspended and bottom sediments and the shoreline (Reed et al., 1999). In order to investigate the influence of the oil spill incident in Singapore Strait, a 3D Lagrangian oil spill numerical model (Brovchenko et al. 2003) - OilTox - is employed to numerically study the oil slick propagation. This model is meshfree and can be used with any model of circulation and waves. It includes oil weathering modelling, deterministic and stochastic oil transport modelling and backtracking modelling.

We carried out series scenarios for different oil spill locations to investigate the oil effect area and the oil concentration distribution during the northeast monsoon season. During northeast monsoon season, the dominant hydrodynamic flow in the Singapore region is from east to west. With these met-ocean forces, spilt oil tends to move toward to the west other than to the east. For the oil spill location near the southwest of Singapore scenario, the oil will affect most of the south coast of Singapore within 3 days (See Figure 1) and the oil concentration near the south coast is around O(0.01) g/L (See Figure 2).

For the oil spill location near the east of Singapore scenario, the oil will arrive at the south coast of Singapore more than 4 days and the oil concentration will be smaller than the former scenario. This investigation of oil slick propagation and the oil concentration will give a reference for the predicting the influence area and extent of oil spill incident in Singapore Strait which is useful for the quickly emergency responding to the oil spill incident.

Validating Formulas for the Prediction of Ascent Speed and Mass Transfer Coefficient for Liquid Oil Droplets and Gas Bubbles under Pressure

J. Gros[1], C. M. Reddy[2], S. A. Socolofsky[3], J. S. Arey[1]
[1]EPFL, Lausanne, Switzerland, [2]WHOI, Woods Hole, MA, [3]TAMU, College Station, TX

Several different formulas exist to predict the ascent speed of gas bubbles and oil droplets released in deep waters. Similarly, different formulas are also available to predict the mass transfer coefficient of compounds dissolving into water during ascent. However, the formulas used by different authors for the modeling of the ascent and mass transfer processes of liquid oil droplets or gas bubbles under pressure can lead to widely different predictions. In this work, we investigate the abilities of different formulas to reproduce literature laboratory data for the ascent speed and mass transfer coefficient for liquid droplets and gas bubbles under pressure. We found that the ascent speed is usually well predicted by a combination of formulas by Clift et al. (1978) or by the Fan-Tsuchiya equation, with mean errors <20% and <25% for liquid CO2 droplet data by Bigalke et al. (2007). The mass transfer coefficient describing transfer of material from “dirty” droplets to water is well reproduced for droplets with diameters in the range 1.5-4 mm by a set of formulas presented in Clift et al. (1978), based on data from Thorsen and Terjesen (1962) for droplets constituted of a mixture of benzene and chlorobenzene. The formula of Kumar and Hartland (1999) behaves satisfactorily for clean droplets.

Trajectory Modeling in support of the Texas City “Y” Oil Spill Response

A. MacFadyen, G. Watabayashi, D. Simecek-Beatty, J. Lankford
NOAA, Seattle, WA

On March 22, 2014 a collision between a cargo vessel and tank barge in in the Houston Ship Channel resulted in a discharge of approximately 4,000 barrels (168,000 gallons) of RMG 380, a heavy fuel oil. NOAA’s Office of Response & Restoration provided forecasts of the oil movement to support the emergency response. Initial predicted shoreline impacts were within Galveston Bay along the north side of the Texas City Dike and along north facing shorelines of Bolivar Roads. However, both model results and overflight observations also indicated a substantial portion of the oil moving offshore into the Gulf of Mexico under the influence of ebb tidal currents and a shift to northerly winds due to a passing cold front. Trajectory forecasts were critical in providing advance warning of future shoreline impacts to the SW on Matagorda Island - a forward operating base was established in this region prior to the oil coming ashore on 27 March. Limitations of the modeling included the inability to resolve small scale circulation within the entrance to Galveston Bay and the failure to predict further longshore transport of tarballs which resulted in sporadic impacts to South Padre Island.

Volume Flux Measurements in the Zone of Flow Establishment of an Aerated Plume

C. C. Lai, S. A. Socolofsky
Texas A&M University, College Station, TX

In the integral plume modeling of oil/gas blowouts, the volume flux emerged at the end of zone of flow establishment (ZFE) is needed to march the parabolic model forward in time. Measurements of the volume flux inside the ZFE are scarce/even non-existent and modelers initialize the model by assuming the plume to have reached an asymptotic densimetric Froude number at the end of ZFE, from which the starting plume velocity can be calculated. In this study, we present a technique that measures the total volume flux at a given plume elevation. It is based on the titration between permanganate ions and thiosulfate ions. An aquarium airstone injects compressed air into a 1x1x1m water tank filled with thiosulfate solution with a known concentration. A collar diffuser is mounted just above the gas release point and injects a known concentration of permanganate solution into the developing plume at a steady flowrate. As the plume rises, it entrains ambient fluid that reacts with the purple permanganate ions. A colorless line will appear at the elevation where the total entrained flow just neutralizes the injected permanganate. By varying the concentration of permanganate ions, we can obtain measurements at different plume elevations inside the ZFE.

Potential Subsurface Plume Formation and Fate in Ultra-deepwater Blowout Simulations Using BLOSOM (Blowout and Spill Occurrence Model)

L. Sim[1], K. Rose[1], J. Graham[2], R. Duran[1], J. Nelson[1], J. Umhoefer[1], J. Vielma[1]
[1]National Energy Technology Laboratory, Albany, OR, [2]Humboldt State University, Arcata, CA

With expanding offshore frontiers into deepwater and ultra-deepwater regions comes the potential for the development of subsurface oil plumes following a blowout or spill event. Subsurface plumes are more difficult to track, generally undergo less degradation, and may either surface much later or potentially settle on the ocean floor. The exact formation rates and subsequent behavior of these plumes are not well known but an attempt was made to simulate and better understand them using BLOSOM, a newly-developed and comprehensive deepwater and ultra-deepwater blowout and spill model developed at the National Energy Technology Laboratory.

This study explored the effects of droplet-size distributions on subsurface plume development and behavior through the explicit handling different droplet-sizes classes and modeling terminal buoyant velocity, the presumed major drivers for subsurface plume formation. Preliminary results show that while smaller droplet-size distributions may initially constrain the surface spill extent and amount of oil beachings, the resultant subsurface plumes increased the duration of the spill as well as both increased the range of affected areas - in some cases with large amounts of settling on the ocean floor - while reducing overall degradation of the crude. It is worth nothing that the model currently does not model biodegradation which certainly plays a large role in degradation of subsurface plumes. However, such results can still provide key insight into the best-use application of subsea dispersants and strategies to mitigate and prepare for potential risks due to subsurface plumes.

GCxGC Comparison of Deepwater Horizon Crude and Kirby Intermediate Fuel Oil (IFO)

R. K. Nelson, R. Swarthout, H. Koolen, C. M. Reddy
Woods Hole Oceanographic Institution, Woods Hole, MA.

On March 22, 2014 the cargo ship Summer Wind collided with a barge owned by Kirby Inland Marine releasing 170,000 gallons of a sticky refinery product known as Intermediate Fuel Oil (IFO). This spill impacted approximately 200 miles of coastline from Texas City (in Galveston Bay) to South Padre Island near Corpus Christi (including the Matagorda Island Wildlife Sanctuary). Using comprehensive two-dimensional gas chromatography (GC×GC) we compare crude oil from the Deepwater Horizon spill with a refinery product (the Kirby IFO). Although smaller in scale than the Deepwater Horizon spill, the Kirby spill offered the chance to study environmental weathering of a refined petroleum product. We collected approximately 200 discrete samples from Galveston to Mustang Island over the course of 4 months and the results of our efforts are presented here. This study adds to our existing work on the Deepwater Horizon spill as we are now able to compare weathering characteristics of crude and refined petroleum products in the Gulf of Mexico.

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

Social Support, Race, and Psychological Distress among Women in the Women and Their Children's Health Study (WaTCH) Exposed to the Deepwater Horizon Oil Spill (DWOS)

S. Gaston, E. Peters, E. Oral, **E. Trapido**, A. Rung
Louisiana State University Health Sciences Center, New Orleans, LA

Previous research has shown that individuals exposed to oil spills are more likely to experience psychological distress; however, social support is thought to buffer these effects. Additionally, cultural differences are thought to affect both appraisal of stressful events and psychological outcomes. The WaTCH Study follows a cohort of Louisiana women affected by the DWOS. The goals of this analysis are to determine: (1) if social support acts as a mediator between perception of the impact of the DWOS and psychological distress and (2) if race moderates the effect of social support on psychological distress. Logistic regression models were used to test for the mediating effect of social support on the relationship between perceived oil spill impact and psychological distress, as well as to examine interaction between social support and race. All models were adjusted for age, education, employment, marital status, physical health, and months since DWOS. Social support was a significant mediator in the association between the perceived impact of the DWOS and psychological distress. However, race was not a significant moderator. Women of all races with low perceived social support were 3.03 times as likely (95% CI: 2.27-4.05) to have symptoms of psychological distress as women with high social support after adjustment for other covariates. Results suggest that social support serves as an important buffer in the exposure to oil spill-psychological distress mechanism.

What Does It Mean? - Lessons from Toxicological Investigation of Crude Oil-Dispersant Impacts on Ecological and Model Organisms

X. Pan
East Carolina University, Greenville, NC

As the crude oil remains a vital natural resource for the energy need of the world, environmental crude oil spills, occurring at different scales, continues to be a health risk to humans and ecological systems. There is a large and growing body of literature reporting the toxicological findings of crude oil-dispersant effects on ecological and experimental model organisms, especially since the Deepwater Horizon oil spill on 2010. Understanding "what does it mean" of current published works would be is an important step towards the evaluation of human health risks and resilience, and the development of targeted diagnostics and prevention strategies. This presentation aims to concisely review the current literatures on various effects of crude oil-dispersant system on organisms' health, and to highlight the transferable biological knowledge and basic principles of interspecies extrapolation. The system-based approaches, such as the utilization of high-throughput technologies to determine interplay between genotype and phenotype, and the need to understand biological pathways and mechanisms of effects will also be discussed.

Risk Assessment of Remnants of Dioctyl Sodium Sulfosuccinate (DOSS) Following Deepwater Horizon Oil Spill: Should We Be Concerned?

O. Ogunsakin
Tulane University, New Orleans, LA

Following Deepwater Horizon (DWH) oil spill disaster which released approximately 210 million US gallons of light crude oil into Gulf of Mexico, an unprecedented amount of dispersants (1.84 million US gallons) were applied to surface and subsurface waters. A major component of the dispersant mixture (Corexit 9527 and Corexit 9500A) was surfactant Dioctyl Sodium SulfoSuccinate (DOSS). DOSS has unique properties of lowering the interfacial tension between water and oil. This loss of cohesion prevents formation of large oil molecules on water surface. Four years after the disaster and response, new studies have shown that DOSS was not removed as expected by biodegradation. This has led to persistence of large compounds of oil-dispersant mixtures in the waters, thus bringing to fore concern about toxicological impact of the remnants of the dispersants. It is also pertinent to know if these oil, dispersants and oil-dispersant mixture are present in concentrations that are potentially toxic to marine life and ultimately humans, especially exposed populations? With established toxicity limits of DOSS among marine life, more investigations will help to evaluate the potential toxicity of the dispersants and its mixture among humans. This research reviews the risk and safety concerns of exposed populations with respect to the overall health effects of DWH oil spill disaster and response, especially as it relates to the use of an unprecedented amount of dispersants, DOSS.

An Assessment of Petrogenic PAH Toxicity in Gulf Shellfish and Finfish using CALUX and Benzo[a]Pyrene Toxic Equivalency

D. Jackson, H. Fernando, G. Ansari, C. Elferink
University of Texas Medical Branch, Galveston, TX

The Gulf Coast Health Alliance: health Risks related to the Macondo Spill (GC-HARMS) consortium is conducting a longitudinal assessment of petrogenic polycyclic aromatic hydrocarbons (PAHs) contamination in Gulf shellfish and finfish species following the 2010 Deepwater Horizon disaster. This is a community-based participatory research project addressing community concerns over seafood safety in the wake of the oil spill. While much is known about the human health concerns associated with environmental contamination by pyrogenic PAHs, little is known about their toxicology as a component of crude oil, and in particular weathered oil. We report data obtained using the EPA approved in vitro CALUX (Chemically Activated LUciferase gene eXpression) bioassay. This assay is based on Aryl Hydrocarbon Receptor activation of a luciferase reporter as a quantitative measure for the presence and biological potency of toxic environmental contaminants. PAHs containing seafood were extracted using validated methods, and used to treat Hepa1 cells stably expressing the Aryl Hydrocarbon Receptor-inducible 1.1 reporter. The seafood derived extracts were compared to standard curves generated with benzo[a]pyrene (BaP) to calculate BaP toxic equivalencies. The analysis compared samples obtained from regions affected by the spill (LA, MS, AL) against extracts obtained from control samples (Galveston, TX) not directly affected by the Deepwater Horizon spill. The data from these experiments have provided a geographical and longitudinal assessment of PAH contamination in Gulf of Mexico seafood, and have been used to inform safe consumption guidelines for our community partners.
Supported by U19ES020676 to CJE.

Deploying Community Health Workers to Bolster Community Resilience

L. Fox, **H. Covert**, S. Denham, M. Lichtveld
Tulane University, New Orleans, LA

Communities that are at risk for natural and technological disasters have begun to embrace community engagement strategies as a means to build community resilience. Research has shown that a community's ability to recover post-disaster is dependent upon the number and quality of social ties between residents and community-based organizations (CBOs). Also, the literature suggests that disaster resilience is improved by ensuring better access to primary care, specifically for vulnerable populations that may be geographically, culturally or linguistically isolated. To that end, the Environmental Health Capacity and Literacy Project (EHCLP) seeks to facilitate connections and improve access to care by deploying community health workers (CHWs) in 13 federally qualified health care centers and CBOs located in communities affected by the Gulf of Mexico oil spill along coastal areas of Louisiana, Mississippi, Alabama and the Florida panhandle. The CHWs offer services that include translation and language access, culturally appropriate health education, helping patients establish a medical home, outreach and insurance enrollment assistance, emergency preparedness, and safety training and resources. The poster will discuss the strategies and metrics that EHCLP uses to evaluate how CHWs are improving access to primary care. Moreover, the poster will discuss lessons learned from the evaluation process, how evaluation data can be used, and suggestions for future evaluation activities.

Can Tributyltin Be Used as a Positive Control for Obesogenic Exposure in the American Alligator?

M. C. Bernhard[1,2], L. J. Guillette, Jr.[3,2], S. Kohno[3,2]
[1]College of Charleston, Charleston, SC, [2]Hollings Marine Laboratory, Charleston, SC, [3]Medical University of South Carolina, Charleston, SC

The US and other developed countries have experienced a rapid increase in obesity. While traditional views associate weight gain with overeating and a lack of exercise, a recent 'obesogen hypothesis' suggests that developmental exposure to certain chemicals could cause obesity later in life. Fractions of MC252 oil, oil/COREXIT and COREXIT alone were identified to be obesogenic in human stem cell assays by our team members. Obesogens activate the peroxisome proliferator-activated receptor gamma (PPARγ) - retinoid x receptor alpha (RXRα) heterodimer, which together stimulate adipogenesis. One obesogen is tributyltin (TBT), which is an agonist for PPARγ-RXRα in mammals. This, however, has not been tested in non-mammalian amniotes, such as non-avian reptiles. The American alligator has been investigated for endocrine disruption as a sentinel species because it exhibits temperature-dependent sex determination (TSD), which is very sensitive to endocrine signaling during development. To investigate the effects of developmental exposure to an obesogen, alligators were exposed in ovo to TBT prior to the thermosensitive period for TSD. Toxicity and a hatchout delay were observed in TBT-treated eggs, but no effects of the obesogen exposure have been observed. In vitro transactivation assays for alligator PPARγ-RXRα will be tested. These results will reveal whether the American alligator can serve as a good sentinel species for the long-term impacts of oil spill contamination.

The Contributions of Gender and Temperament to Self-Reported Resilience after the Gulf of Mexico Oil Spill

R**. Jollie**[1], L. Baker[1], B. Brumback[2], S. Roberts[1], A. Cohen[1], L. Grattan[1], G. Morris[2]
[1]University of Maryland School, School of Medicine, Baltimore, MD, [2]University of Florida, Gainesville, FL

Resilience refers to the ability to successfully adapt to adversity or a stressful life event. The Gulf of Mexico oil spill disaster and related stressors represented a negative life event for many NE Gulf Coast residents. This event provided a unique opportunity to study resilience and many other factors that could potentially contribute to or moderate the process. Since gender differences have been previously found in studies of disaster recovery (Norris et al., 2002), it was also examined as a potential moderating factor of the relationship between temperament and resilience. Temperament, gender, and self-reported resilience outcomes were studied in 26 men and 62 women who resided in NE Gulf Coast Communities. Measures included the Connor-Davidson Resilience Scale (Connor & Davidson, 2003) and the Adult Temperament Questionnaire (Evans & Rothbart, 2007) within the context of a broader psychological evaluation. Results indicated that gender moderated the relationship between effortful self-control and resilience (β = .48, F (3, 84) = 11.71, p < .05), such that there was a stronger positive relationship between effortful self-control and resilience for men (r = .84) than for women (r = .36). A strong relationship was also found between resilience and extraversion (r = .53) and resilience and negative affect (r = -.49), though gender did not moderate these relationships. These findings illustrate the need to further understand the specific dispositional characteristics of individuals who are better able to cope with and adapt to adversity and disaster as well as specific factors that may moderate higher and lower resilience between genders.

Environmental Worry after Oil Spill: Relative Contributions of Anxiety and Gender

S. Roberts[1], L. Baker[1], R. Jollie[1], B. Brumback[2], J. Morris[3], L. Grattan[1]
[1]University of Maryland School of Medicine, Baltimore, MD, [2]University of Florida, Gainesville, FL, [3]University of Florida, Emerging Pathogens Institute, Gainesville, FL

Risk perception is the characteristic way people approach, think about and interpret risks in their environment. After oil spill it involves how a person perceives, understands, and deals with event-related information as well as associated environmental and health risks. Anxiety is often attributed to elevations in risk perception. Gender has also been identified as an important variable in risk perception. This study examined the extent to which an individual's gender and typical level of anxiety contributed to their level of environmental worry after the Gulf of Mexico Oil Spill. Measures of anxiety (State-Trait Anxiety Inventory) and environmental worry (a factor of risk perception measured by the Health and Environment Questionnaire-V) were administered to 109 men and 143 women from two NE Gulf coast communities 2 years post oil spill. Results indicated that Trait anxiety was significant but minimally predicted environmental worry ($\beta = .15$, $F(1,250) = 5.84$, $p<.05$). State anxiety did not significantly predict environmental worry ($\beta = .08$, $F(1,249) = 1.49$, n.s.) Gender, when added to the regression model, was not a significant predictor beyond Trait anxiety alone. In conclusion, individuals with a more stable and enduring sense of anxiety worried more about health and environmental impacts of the GoMOS than those who were more reactive. Men and women with lower levels of observed distress represent a population at risk of high levels of environmental worry.

A Worst Case Scenario Analysis for Economic Impact of Oil Spill Incidence in GOM

N. Dahi, M. Tyagi
Louisiana State University, Baton Rouge, LA

The Deepwater Horizon oil spill, the largest marine oil spill in history, was caused by an explosion on a semi-submersible drilling rig on April 20, 2010. Catastrophic events such as oil spills have enormous impact for the local economy of the area and even for the local labor markets. Another provincial disaster, Hurricane Katrina impacted Louisiana, Mississippi, and Alabama, as it ripped over the core of the Gulf of Mexico producing zone. The deepwater rigs located in the Gulf of Mexico are responsible for the employment of over 700 workers per rig, especially impacting tax revenue to the state of Louisiana (GNO, Inc. 2011).

Whenever a disaster happens, another reaction to this event that should be considered is resiliency. It is ability to reduce or remove potential losses due to disaster events. Louisiana was most significantly impacted, being a state that relies heavily on oil and gas industries in the Gulf of Mexico. With continued developments of drilling and production in deepwater, it remains very critical to have a broad and quantitative risk assessment of the drilling and production processes including effective response to deal with multiple disasters. The impact of different shocks on various aspects of a state's economic performance is estimated using a Vector Autoregressive model (VAR).

Assessing Personalized Exposures of Importance: What We've Learned from Paired Indoor/Outdoor Air Sampling, Seafood Analyses, and Study Design in Southeast Louisiana

J**. L. Howard**[1], T. Stock[2], E. Overton[3], D. Gauthe[4], D. Nguyen[5], M. Wilson[1], J. Wickliffe[1]
[1]Tulane University, New Orleans, LA, [2]University of Texas, Houston, TX, [3]Louisiana State University, Baton Rouge, LA, [4]Bayou Interfaith Shared Community Organizing, Thibodaux, LA, [5]Mary Queen of Vietnam Community Development Corporation, New Orleans, LA

The Deepwater Horizon accident in 2010 raised concerns regarding negative impacts on air and seafood quality. Though individual perceptions varied, many people in coastal communities in southeast Louisiana felt that they experienced increased exposure to oil- and dispersant-related compounds. 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 are also 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. What we have learned is that preliminary results indicate levels of the selected volatile organic compounds (VOCs) 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. Additionally, through hands-on experience, we have learned the complications associated with in-home, community-based participatory research when conducted in transient, lower-income populations and will discuss methods for enhancing communication and use these lessons to improve future study designs of this type. Finally, we will discuss the correlations and implications of our findings to date and how involving individuals in the risk analysis/assessment process may aid informed decision-making.

Anger, Bitterness, and Social Support as Predictors of Mental Health Outcome Two-Year Post Gulf of Mexico Oil Spill in Residents Who Experienced Income Loss

L. Baker[1], R. Jollie[1], S. Roberts[1], J. Morris[2], L. Grattan[1]
[1]University of Maryland School of Medicine, Baltimore, MD, [2]University of Florida, Emerging Pathogens Institute, Gainesville, FL

While anger and bitterness are considered normal negative emotional reactions to perceived maltreatment and injustice, these negative stress responses can be associated with poor mental health outcome. In contrast, social support has been associated with more positive mental health outcome, included lower depression and anxiety. This study examines anger, bitterness, and social support as predictors of mental health outcome, specifically depression, and state and trait anxiety two-years after the Gulf of Mexico Oil Spill in 112 Gulf Coast residents who experienced income loss. Higher levels of reported anger and bitterness were associated with poorer mental health outcome ($r = .195$ to $.577$), while higher levels of self-reported social support were associated with lower levels of depression, and state and trait anxiety ($r = -.310$ to $-.466$). Anger and social support were significant predictors of mental health outcomes, while bitterness was not a significant predictor. Overall, anger was the strongest predictor of all three mental health outcomes: depression, state anxiety, and trait anxiety (e.g., $\beta = .460$, $t = 5.59$, $p < .001$). These findings suggest that interventions focused on decreasing negative emotions and increasing social support may have utility in promoting better mental health outcome in the aftermath of an environmental disaster.

Substance Use in Response to the Deepwater Horizon Oil Spill

L. Cole, **E. Trapido**, E. Peters
Louisiana State University Health Sciences Center School of Public Health, New Orleans, LA

BACKGROUND: In 2010, the Deepwater Horizon Oil Spill (DWOS) deeply affected the Gulf Coast, impacting residents both economically and psychologically. Following disasters and traumatic events, such as the DWOS, individuals tend to use alcohol and tobacco as coping strategies. Our objective is to determine the impact of exposure to the DWOS on substance use. METHODS: We utilized the Women and Their Children's Health Study, which has enrolled and interviewed women residing in seven coastal Louisiana parishes affected by the DWOS. To estimate the association between reported oil spill exposure and substance use, we used logistic regression to calculate odds ratios and 95% confidence intervals. We considered age, race and depression as confounders a priori; and evaluated income, education, current employment and marital status as potential confounders. RESULTS: 2,547 women were included in the analysis. The mean age of participants was 46 years, with 57.4% of the women White and 35.3% Black. 27.4% of the women currently drink alcohol and 19.7% are current smokers. Since the DWOS, 9.9% of current drinkers and 33.1% of current smokers reported increases in drinking and smoking, respectively. We observed that women reporting higher oil spill exposure were more likely to currently smoke compared to non-smokers (aOR=1.408, 95%CI=1.13-1.75), and were more likely to report an increase in smoking since the DWOS (aOR=1.948, 95%CI=1.28-2.97). We did not find any significant associations between reported oil spill exposure and alcohol consumption. CONCLUSION: Our data suggests that exposure to the DWOS increased smoking habits, but did not impact alcohol consumption.

A Multi-Level Investigation of Neighborhood Disadvantage and Depression in the Women and Their Children's Health (WaTCH) Study in Louisiana

S. Sullivan, E. Peters, **E. Trapido**, E. Oral, A. Rung
Louisiana State University Health Sciences Center School of Public Health, New Orleans, LA

To determine whether women who lived in disadvantaged neighborhoods were more likely to have depression, data were used from the WaTCH Study (n=2251), a cohort study of the long-term health effects of women exposed to the Deepwater Horizon oil spill. Census tract data (crime risk, percent in poverty, percent on public assistance, percent of female headed households, and percent unemployed) were merged from the 2012 American Community Survey. Neighborhood variables were standardized and summed so that higher scores indicated greater disadvantaged neighborhoods. Scores ≥ 16 on the Center for Epidemiologic Studies Depression Scale (CES-D) indicated depression. The mean age of women was 46 years, 57% were White, 12% had less than a high school education, and mean oil spill exposure was 1.4 (SD 1.1). Multi-level logistic regression models were used to obtain odds ratios (OR) for depression. The median odds ratio (MOR) of 1.26 suggests 26% of the variance in depression may be attributed to differences due to neighborhood disadvantage. After adjustment for age, oil spill exposure, race, and education, women who lived in higher disadvantaged neighborhoods had an increased odds of depression (OR: 1.09; 95% CI: 1.01, 1.17) and the MOR was 27%. Increasing oil spill exposure was also significantly associated with depression (OR: 1.15, 95% CI: 1.05, 1.27). These data show that for women in Louisiana, disadvantaged neighborhoods may have an important relationship with depression.

Mental and Behavioral Health Effects of the Deepwater Horizon Gulf Oil Spill: Anxiety, Resilience, Treatment Methods, and Future Recovery

A. Speier, H. Osofsky, J. Osofsky, T. Hansel, J. Wells, C. Weems, L. King, G. Fassnacht
Louisiana State University Health Sciences Center, New Orleans, LA

The interconnectedness of people and environment is fundamental to human development, and the aspirations of individuals. The vulnerability of this ecosystem became evident following the Deepwater Horizon (DWH) Gulf Oil Spill. Anxiety which was directly attributed to the oil spill affected both adult and younger populations and remained elevated for over 3 years. The LSUHSC Department of Psychiatry has been accessing these ecological impacts on mental health since 2010. Medication, brief CBT-informed interventions, individualized care management, and school based services have resulted in decreased symptoms. This paper presentation will report on the presence and treatment strategies used to address the impact of elevated anxiety levels across the population and discuss long-term implications on health and psychological well-being. The presentation will: (1) present data collected on adults and school children demonstrating post oil spill levels of anxiety; (2) discuss methods currently being implemented in primary health care clinics and public schools in efforts to decrease these symptoms; (3) present data revealing the decrease in anxiety and increase in resilience following services; and (4) discuss how these surveillance and intervention strategies can be used to assess, treat, and assist communities to recover from the mental and behavioral health effects following future extreme ecological incidents.

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

Interannual Recruitment Dynamics for Resident and Transient Marsh Species: Evidence for a Lack of Impact by the Macondo Oil Spill

J. Cebrian, R. Moody, K. Heck, A. Macy
Dauphin Island Sea Lab, Dauphin Island, AL

The emulsification of oil at the Deepwater Horizon (DWH) well head relegated a large proportion of resultant hydrocarbon plumes to the deep sea, facilitated the incorporation of oil droplets into microbial and planktonic food web, and limited the severity of direct, wetland oiling to coastal Louisiana. Nevertheless, many transient fish and invertebrate species rely on offshore surface waters for egg and larval transport before settling in coastal habitats, thereby potentially impacting the recruitment of transient species to coastal nursery habitats quite distant from the well site. We compared the utilization of salt-marsh habitats by transient and resident fishes and invertebrates before and after the DWH accident using data obtained from an oyster reef restoration project in coastal Alabama. Overall, we did not find significant differences in the recruitment of marsh-associated resident and transient nekton in coastal Alabama following the DWH accident. Our negative findings are consistent with other assessments of nekton in coastal vegetated habitats and bolster the notion that, despite the presence of localized hydrocarbon enrichments in coastal habitats outside of Louisiana the most severe oil impacts were relegated to coastal Louisiana and the deep sea.

A Simulation Analysis of the Plankton Fate of the Deepwater Horizon Oil Spills

J. J. Walsh[1], **J. M. Lenes[1]**, B. P. Darrow[1], A. A. Parks[1], R. H. Weisberg[1], L. Zheng[1], C. Hu[1], B. B. Barnes[1], K. L. Daly[1], G. R. Brooks[2], W. H. Jeffrey[3], R. A. Snyder[3], D. J. Hollander[1]
[1]University of South Florida, St. Petersburg, FL, [2]Eckerd College, St. Petersburg, FL, [3]University of West Florida, Pensacola, FL

A two-dimensional (2-D) ecosystem model, set within the De Soto Canyon ecotone of the Northern Gulf of Mexico (NGOM) and driven by 3-D flow fields from coupled circulation models, explores the daily food web and sedimentary consequences of oil, nutrient, and plankton induced transitions of dominant particle transports to the sea floor from vectors of copepod fecal pellets to those of marine snow over the annual period of 2010-2011. Spilled petrochemicals are found to both decimate zooplankton populations and facilitate formation of marine snow macro-aggregates. During descent of modeled marine snow to the ~1200-m isobath of the upper slope, ~90% of the particulate import to the benthos is clay minerals of Mississippi River origin on the western side of the ecotone, scavenged by marine snow from the water column. The model results here replicate concurrent time series of: 1) annual sediment accumulations, measured at the sea floor; 2) bimonthly onshore nutrient supplies due to upwelling, forced remotely by the Loop Current; and 3) near-surface weekly phytoplankton changes, seen by satellite. The model calculates the relative contributions to sedimentary mass accumulation rates after the Deepwater Horizon oil spills as: decreased herbivory = 8%; Mississippi River nutrients loadings = 12%; oiled marine snow = 30%; and ungrazed phytoplankton entrained within marine snow = 50%, where the elevated phytoplankton biomass was fueled by anomalies of increased nutrient supplies from Loop Current driven upwelling.

Nutrient Concentrations along the River Plume Salinity Gradient in the Northern Gulf of Mexico over the Past 30 Years

A. Bracco[1], Y. Cardona[1], T. Villareal[2], A. Subramaniam[3], S. Weber[4], J. Montoya[4]
[1]EAS - Georgia Tech, Atlanta, GA, [2]MSI - University Texas Austin, Port Aransas, TX, [3]LDEO, Palisades, NY, [4]School of Biology - Georgia Tech, Atlanta, GA

The distribution of surface nutrients along the salinity gradient in the Mississippi-Atchafalaya River outflow region is examined following a series of four cruises conducted in the Northern Gulf after the Deepwater Horizon blowout in late spring and summer of 2010, 2011, and 2012. The new, extensive data set covers the salinity gradient from 11 to 37 psu, in years of average (2010, 2012) and extraordinarily high (2011) river discharge, as well as during different stages of the Loop Current extension. The overall concentrations of nitrate + nitrite, orthophosphate and silicate are compared to those recorded in cruises spanning the 1985 - 2009 interval. Using Monte Carlo simulations to test the statistical significance, concentrations of orthophosphate and nitrate and nitrite are found to be different in the 2010-2012 period compared to the previous years. Their means decreased by approximately three and two folds, respectively. Changes in silicate are less dramatic and their statistical significance is uncertain. The river loading of these four nutrients, on the other hand, does not display any significant trend, except for a 10-15% decrease in nitrate/nitrite, suggesting that nitrate/nitrite and orthophosphorus utilization in the ocean may have increased in the most recent period.

Intra-specific Differences in the Food Resources used by Seaside Sparrow (*Ammodramus maritimus*): A Consequence of Prey Availability?

J. A. Olin, C. M. Bergeon Burns, W. Bam, L. Hooper-Bui, S. Taylor, P. Stouffer
Louisiana State University, Baton Rouge, LA

The flow of energy to higher trophic levels is largely dependent on available prey resources and any changes in this resource may have important consequences for species fitness, as well as the structure and function of the overall food web. Declining abundances of terrestrial arthropods observed following the Deepwater Horizon oil spill have the capacity to alter trophic interactions of resident terrestrial salt marsh species, posing challenges to the diversity and function of these communities. The Seaside Sparrow (*Ammodramus maritimus*) is a common passerine species in Gulf coast marshes that mainly forages on terrestrial arthropods, serving as an indicator species to the broader terrestrial food web response to disturbance. In this study, changes in the ratios of stable nitrogen and carbon isotopes and fatty acid profiles were used to trace food web pathways utilized by Seaside Sparrow breeding across a gradient of oiled and unoiled marshes along the Louisiana coastline. These profiles were then compared with estimates of available terrestrial arthropod prey from each site. Our findings will provide insights into resource exploitation pathways of Louisiana Seaside Sparrows in response to anthropogenic disturbance and will aid in identifying factors contributing to the poor nest success observed for individuals residing on oiled marshes.

Transcriptional Responses of Blue Crabs and Bay Anchovies to Surrogate Oil

B. Yednock[1], T. Duffy[2], T. Sullivan[3], E. Chesney[4], **J. Neigel[3]**
[1]South Slough National Estuarine Research Reserve, Charleston, OR, [2]Northeastern University, Boston, MA, [3]University of Louisiana at Lafayette, Lafayette, LA, [4]Louisiana Universities Marine Consortium, Chauvin, LA

The blue crab (*Callinectes sapidus*) and bay anchovy (*Anchoa mitchilli*) are abundant, ecologically important species in the northern Gulf of Mexico. We are currently investigating how oil spills impact their vulnerable early life stages. As part of these investigations, we have experimentally determined how patterns of gene expression change following short-term exposures to oil. Juvenile blue crabs and larval bay anchovy were separately exposed for 24 hours to sub-lethal concentrations of a water accommodated fraction (WAF) of the surrogate for Macondo crude oil. In comparison with controls, exposure to oil produced significant changes in both overall levels of expression and patterns of transcriptional splicing for genes with functions relevant to metabolism of xenobiotic compounds and general stress responses. For example, in blue crabs there was a large increase in expression a glucosyl glucuronosyltransferase, which in mammals plays a key role in detoxification of xenobiotic compounds. Real-time PCR was used to validate a subset of these responses. These experiments provide insights into the physiological responses and detoxification pathways engaged following exposure to oil, and their possible role in adaptation to oil and other pollutants.

Gulf of Mexico Marine Organism's Susceptibility to Photo-enhanced Toxicity of Fluoranthene at Different Life Stages and Ultraviolet Light Intensities

B. E. Finch, W. A. Stubblefield
Oregon State University, Albany, OR

Organisms have developed defense mechanisms to cope with damaging effects of ultraviolet (UV) light over evolutionary time including photoreception, photorepair, and avoidance. Some early life stage aquatic organisms are predicted to be more susceptible to photo-enhanced toxicity if they are translucent and found in shallow water habitats. The objective of this study was to evaluate the photo-enhanced toxicity of fluoranthene and pigmentation in varying life stages of mysid shrimp, inland silverside, sheepshead minnow, and Gulf killifish. In addition, photo-enhanced toxicity was compared among a high UV intensity, short duration study (4 h) conducted at 24 W/m2 UV-A and a low UV intensity, long duration (12 h) study at ~8 W/m2 UV-A. Susceptibility of organisms to photo-enhanced toxicity was determined by comparing median lethal concentrations (LC50s) and elapsed time to 50% mortality (LT50s). Data demonstrated organisms become increasingly resistant to photo-enhanced toxicity with increasing age, evident by increased survival and time-to-death. The amount of pigmentation in organisms correlated with observed LC50 and LT50 values, suggesting that increased pigmentation is a protective mechanism against photo-enhanced toxicity. Fluoranthene LC50s of low and high UV light intensities were significantly different for all organisms with the exception of Gulf killifish. Data suggests photo-enhanced toxicity is dependent on organism's life stage, pigmentation, UV light intensity, and fluoranthene concentration.

Investigating the Impact of the Deepwater Horizon Oil Spill on Mercury Concentrations in Northern Gulf of Mexico Fishes

A. R. Harper[1], V. Eller[1], V. Perrot[2]
[1]Florida State University, Tallahassee, FL, [2]National High Magnetic Field Laboratory, Tallahassee, FL

The large input of organic material from the Deepwater Horizon oil spill resulted in local scale conditions that potentially promoted the formation of methylmercury (MeHg) and, based on our research, has increased the mercury levels in some fish. To test the hypothesis that DWH resulted in higher Hg levels in Gulf of Mexico fish species we first assessed the linkage between MeHg concentration and the strength of the reduced-sulfur stable isotope δ34S signal in coastal consumer organisms and found that where δ34S was most depleted, fish Hg concentrations were highest. This finding indicates that MeHg loads of coastal organisms results from dissimilatory sulfate-reduction in near-shore sediments. Next, we analyzed commercially important reef fish species and compared them to a sample-set collected in 2009-10 to determine whether Hg concentrations have increased following DWH. Finally, to better understand the geographic distribution, sources, and in-vivo and environmental processes affecting Hg accumulation in marine organisms we employed Hg stable isotopes analysis.

Polycylic Aromatic Hydrocarbon Concentration and Fish Liver Condition around the Ixtoc-1 Well Area, SW Gulf of Mexico

A. Gracia[1], H. M. Alexander-Valdés[1], A. R. Vázquez-Bader[2]
[1]Instituto de Ciencias del Mar y Limnología, UNAM, Mexico City, Mexico, [2]Instituto de Ciencias del Mar y Limnología, UNAM, México City, Mexico

PAH concentrations in muscle and bilis of 28 fish species and in sediment were analyzed in the vicinity of the Ixtoc location in the SWGoM during 2005 to 2010. Histologycal analysis were also done to examine fish liver condition. Overall PAH concentration ranges found were: muscle 3-198-636.216 µg/kg, bilis 0.021-353.678 µg/kg and sediment 0.348-248.67 µg/kg. Annual PAH muscle, bilis and sediment mean values varied within an order of magnitude (muscle: 14.784-91.689, bilis: 9.063- 54.660, sediment: 15.752-83.076 µg/kg) and showed maximum records in 2010 for sediment and in 2008 for muscle and bilis. PAH muscle and bilis values did not present a correlation with current PAH sediment values. Histopathologycal analysis showed a constant incidence of liver lesions along the whole period which peaked in severity (90%) and frequency (100%) during 2007. Hepatic damage did not show a correlation with either PAH muscle or bilis PAH concentration but it did with the increase of sediment PAH in sampling locations. Annual hepatic damage frequency seems to be affected both by chronic and episodic exposure to hydrocarbons from the oil platform área of the SW GoM. Apparently exposure to episodic events of high levels of PAH concentration may have an increasing direct impact in fish liver which may also have consequences at individual and population levels.

The Combined Effect of Environmental and Anthropogenic Stressors on Fish Health

L. van Balen[1], R. Vroom[1], T. Bosker[1], S. DeGuise[2], C. Perkins[2], M. S. Sepulveda[3], **R. J. Griffitt**[4]
[1]Leiden University College, The Hague, Netherlands, [2]University of Connecticut, Storrs, CT, [3]Purdue University, West Lafayette, IN, [4]University of Southern Mississippi, Ocean Springs, MS

Understanding the impacts of oil and dispersant during early development of fish is of importance, as this has been shown to be a sensitive life stage. In this research we determined the effects of chemically enhanced water accommodated fraction (CEWAF), on the health of embryo and larval sheepshead minnow (*Cyprinodon variegatus*). Embryos (24h post fertilization, 10 individuals per replicate) were exposed in triplicate for 48hrs to two different concentration of CEWAF, and followed until 10 days post fertilization. After 48h, the embryos were placed into clean, uncontaminated water for the duration of the experiment. Treatment effects were assessed using the following indicators: daily heartbeat count, eye pigmentation, embryonic movement, time to hatch, hatch success rate, larval survival, length at hatch, and CYP1A expression at 10 dpf. All endpoints except eye pigment and gene expression showed significant differences compared to control impacted during exposure to CEWAF, indicating that a short duration exposure early in embryonic development can have severe adverse effects that continue after the stressor is removed. This research will contribute in understanding direct effects as well as the potential long-term impacts of oil exposure on larval fish health and population status.

Understanding Spatial Trends in Biliary PAH metabolite Concentration in Gulf of Mexico Demersal Fishes Using Sediment PAH Concentration and Sediment Grain Size

S. M. Snyder[1], E. L. Pulster[2], D. L. Wetzel[2], I. C. Romero[1], R. Larson[3], G. Brooks[3], D. Hollander[1], S. Murawski[1]

[1]University of South Florida, St Petersburg, FL, [2]Mote Marine Laboratory, Sarasota, FL, [3]Eckerd College, St Petersburg, FL

Biliary PAH metabolites quantified in demersal fishes following the Deepwater Horizon blowout revealed intriguing trends in species-specific and spatial differences in exposure to PAH pollution. At each location fish were sampled, sediment cores were taken by multicorer. In this study, we integrate data for biliary PAH metabolites, sediment PAH concentration and sediment grain-size to better explain the observed trends in exposure to PAHs. Analysis of biliary PAH metabolites revealed a burrow-forming fish, golden tilefish (*Lopholatilus chamaeleonticeps*), had significantly higher concentrations of low molecular weight biliary PAH metabolites compared to other demersal species. The high level of interaction between golden tilefish and the sediment, due to incidental sediment ingestion while burrowing, may explain the high PAH concentrations seen in golden tilefish bile samples. When examining differences in biliary PAH metabolite concentrations between locations where golden tilefish were sampled, the station where golden tilefish exhibited the lowest concentrations of biliary PAH metabolites was a gravel dominated sediment site, and consequently, has the lowest sediment PAH concentration from all stations where sediment cores were taken. Gravely sediment may not be suitable for tilefish burrow formation, therefore, tilefish would have one less route of exposure to PAH pollution, explaining the lowest biliary PAH metabolites at that station. If sediment is a route of exposure for these demersal fishes, sediment grain size may be controlling level of PAH accumulation in sediment and in turn, level of exposure.

Further Evidence for the Presence of Deepwater Horizon Oil on the West Florida Shelf

L. D. McDaniel[1], D. Wetzel[2], J. Basso[3], **J. H. Paul**[1]

[1]University of South Florida, College of Marine Science, Saint Petersburg, FL, [2]Mote Marine Laboratory, Sarasota, FL, [3]University of Tennessee, Knoxville, TN

The ecological consequences of the Deepwater Horizon Oil Disaster (DHOD) are both long-term and pervasive. The extent to which shorelines other than those in the Northeast Gulf of Mexico have been impacted remains uncertain. The distribution of toxicity and mutagenicity in the Gulf of Mexico suggests that hydrocarbons from the Deepwater Horizon spill could have contaminated areas along the West Florida Shelf (WFS). However, many of these measurements were made in the absence of hydrocarbon metadata. We have adopted chemical fingerprinting methods including polynuclear aromatic hydrocarbon (PAH) analysis in order to determine the presence and origin of hydrocarbon contaminants in sediment samples from coastal environments. These analyses were performed in conjunction with biological-based toxicity and mutagenicity testing to determine the potential biological consequences of the hydrocarbon contamination. PAH profiles from samples taken from beaches fringing the WFS were found to be statistically significantly similar by two different analytical methods with those of beaches taken from known impacted areas in the Northeast Gulf of Mexico (Gulf Shores, AL and Ft. Pickens, FL). Additionally, some of these samples were found to possess acute toxicity or mutagenicity. These

findings are consistent with observations and modeling of upwelling on the shelf as well as lesions in non-demersal fish collected on the WFS. We therefore conclude that hydrocarbons from the DHOD did find their way on to the WFS.

Benthic Foraminifera as Environmental Proxies for PAH Pollution following the Hercules 265 Event

B. J. O'Malley, P. T. Schwing, I. C. Romero, D. J. Hollander
University of South Florida, St. Petersburg, FL

In July 2013, the Hercules 265 gas rig explosion introduced petrochemicals into the northern Gulf of Mexico (GoM). Sediment cores were collected from three sites along a 10 NM transect, SE of the rig, to assess the amount of petrochemicals introduced into the sediments and potential toxicity to benthic fauna. Benthic foraminifera (BF) can be used as bio-indicators of environmental toxicity due to their high turnover rate and durable carbonate mineral tests, which are preserved well in stratigraphic records. Previous studies have used pollution-resistant pioneer species (*Elphidium excavatum*, *Haynesina germanica*, *Ammonia beccarii*) to identify areas with elevated PAH concentrations (Chatelet, 2003). This study tests the efficacy of BF as bio-indicators of toxicity for short-term (weeks to months) contamination (Hercules explosion) in the context of potential chronic contamination from drilling (years to decades). In the most recently deposited sediments, high molecular weight PAH concentrations, including the carcinogenic and pyrogenically-derived benzo[a]pyrene, decrease outward from the wellhead. Spatial and depth variability in PAH concentrations will be compared to assemblage diversity, and abundance of previously documented pioneer species. This study will shed light on which species of BF are PAH-tolerant indicators for future identification of PAH pollution in benthic habitats. Population changes of low-trophic level organisms, like BF, can directly affect higher-level consumers and impact the structure and function of the ecosystem.

Imprint of the Deepwater Horizon Oil and Methane Carbon in Suspended Particles in the Gulf of Mexico

A. Fernández[1,2], S. C. Weber[1], J. P. Montoya[1]
[1]Georgia Institute of Technology, Atlanta, GA, [2]Universidade de Vigo, Vigo, Spain

In 2010, the Deepwater Horizon (DWH) blow-out resulted in the release of an unprecedented amount of 13C depleted oil and gas to the Gulf of Mexico (δ13C -27‰ and -57‰, respectively), which moved both as surface slicks and as deep, horizontally driven plumes at 1000-1200m depth. Between 2010 and 2012, we conducted 5 research cruises to study the impact of that oil and gas carbon in the offshore systems affected by the DWH. Here we report on the δ13C of suspended particles, which provides insight into the carbon sources supporting the microbial food web. In 2010, low δ13C (<25‰) values in particles at 1000-1200m depth suggest that incorporation of methane-C could account for up to 25% of particulate carbon at those depths, a greater impact than we observed near the surface. In 2011, low δ13C values were distributed evenly throughout the water column, suggesting that the petro-carbon was still recycling through the microbial food web. In 2012, we found low δ13C values throughout the water column around the DWH site. We also observed surface oil slicks attributed to leakage from the DWH containment dome, suggesting continuing inputs of oil to the area. Our data document the rapid response of microbial communities to the input of gas and oil into the water column, leading to

significant incorporation of petro-carbon into the pelagic food web and a biogeochemical impact that may persist for years.

Phytoplankton Associations in the Northeastern Gulf of Mexico: Vertical Profiles between Pensacola Bay and DeSoto Canyon

J. A. Nienow[1], C. M. Bryller[1], T. S. Dinkins[1], C. D. Horruitiner[2], M. N. Waters[1], S. Wise[3]
[1]Valdosta State University, Valdosta, GA, [2]University of Florida, Gainesville, FL, [3]Florida State University, Tallahassee, FL

Phytoplankton associations in the northeastern Gulf of Mexico are dependent on the complex interactions of Loop Current eddies, prevailing winds, plumes from the Mississippi, and upwelling over the shelf break and through DeSoto Canyon. To better understand this system, we are working as part of a multidisciplinary project aimed at the development of models explicitly describing the interactions of the physical and biological systems in the region. Here we report on vertical profiles developed from samples collected May, 2012, and June, September, and December, 2013. Samples were collected from 5 stations along a 75-km transect extending from Pensacola Bay. At each station 1-liter samples were collected at regular intervals to depths of up to 200 m. The samples were filtered onto 0.45 µm nitrocellulose filters and air-dried. Estimates of the numbers of diatoms, coccolithophorids, and armored dinoflagellates were made at the lowest taxon possible using SEM. In all sampling periods a distinct subsurface association formed in off-shore stations, consistent with a flow of nutrient-rich water up the canyon and onto the shelf. The composition of both the surface and subsurface association changed with sampling period, highlighting the complexity of the system and the difficulty in distinguishing the impacts of individual events after the fact. In order to address this issue, we plan to expand our analysis by examining archived samples collected during cruises conducted during 2011 & 2012 and by working with members of the modeling team to put the profiles in a physical context. We are also investigating the use of pigment analysis and imaging flow cytometry to increase the rate of analysis after future cruises.

Nematode Community Structure in Northern Gulf of Mexico Continental Shelf Sediments following the Deepwater Horizon Oil Spill

C. C. Martinec[1], J. Sharma[2], J. M. Miller[1], P. M. Stewart[1], S. C. Landers[1]
[1]Troy University, Troy, AL, [2]University of Texas San Antonio, San Antonio, TX

This study analyzed marine nematode communities on the Gulf of Mexico (GOM) continental shelf. Sediment cores were collected in fall 2012 from central Louisiana to Apalachicola, Florida at depths ranging from 49–361 m. Heavy metals, organic carbon, and sediment granulometry were determined for each site. Twenty-six genera not found in recent GOM checklists were documented in this study. The two dominant genera were *Dorylaimopsis* (13% of total) and *Sabatieria* (8.1%). The dominant feeding types were selective deposit feeders (35.1%) and episubstrate feeders (35.1%). Spearman's rank correlation analysis revealed that *Sabatieria* abundance correlated negatively with medium sand ($p = 0.005$) and positively with silt + clay ($p = 0.013$). Episubstrate feeders correlated negatively with depth ($p = 0.002$) and positively with temperature ($p = 0.002$) and dissolved oxygen ($p = 0.036$). Univariate correlations between nonmetric multidimensional scaling axes and abiotic variables suggest that metals and sediment grain size were most closely related to nematode community structure. Principal components (PC's) 1, 2, and 3 of metals explained nearly 99% of the total variance, while PC1 (a

component comprised of all metals) positively correlated with nematode communities. BIOENV showed that Al and Cu (ρ = 0.552) had the highest correlation to nematode similarity data. These metals significantly correlated with other trace metals and are attributable to natural clay minerals. Very fine sand, silt + clay, and organic carbon had the next highest correlation (ρ = 0.455) to nematode similarity data, indicating that nematodes may prefer certain sediment grain sizes. This research was made possible by a grant from BP/The Gulf of Mexico Research Initiative.

Phytoplankton Associations in the Northeastern Gulf of Mexico: Changes in the Net Plankton Association, 2011 - 2014

C. M. Bryller[1], J. A. Nienow[1], S. Wise[2]
[1]Valdosta State University, Valdosta, GA, [2]Florida State University, Tallahassee, FL

The Macondo blow-out almost certainly had an immediate impact on the structure of the plankton association in the northern Gulf of Mexico. The extent and duration of the impact are not as clear. Here we report on our preliminary analysis of net plankton samples collected during 19 cruises conducted between January, 2011, and June, 2014, along transects extending up to 80 km from the coast of Florida to the head of DeSoto Canyon. At each station, net-plankton (vertical tows of up to 100 m, using a 25µm mesh net) samples were collected for the analysis of larger forms. The relative abundance of each of 12 categories (*Ceratium* spp., *Dinophysis* spp., other dinoflagellates, Rhizosoleniaceae, Chaetocerotaceae, Hemiaulaceae, Thalassionemataceae (*Thalassionema* spp.), Bacillariaceae, other chain-forming diatoms, other diatoms, cyanobacteria (*Trichodesmium*), and zooplankton), was determined by light microscopy. The results suggest that the association was subject to dramatic fluctuations marked by reduced diversity and the dominance of individual groups during the first half of 2011 to a greater degree than was evident in subsequent years. We plan to work with ecosystem modelers to see whether the observed fluctuations in the structure of the association can be explained by naturally occurring changes in the physical/chemical environment or represent an echo of the impacts caused by the blow-out.

Composition and Quantity of Calcareous Nannoplankton Assemblages Present during the 2010 Macondo Oil Spill in the Gulf of Mexico

A. E. Agbali[1], A. J. Avery[2], J. W. Cruz[2], S. W. Wise[2]
[1]Florida State University, Tallahassee, FL, [2]FSU, Tallahassee, FL

Calcareous nannoplankton are important photosynthetic protist constituents at the base of the food chain in the Gulf of Mexico, however, no quantitative studies have yet been published on their abundance and seasonal variability in this region. Thus, the effects of the BP Macondo Oil Spill from April 20 to July 15, 2010, on these skeletal-bearing phytoplankton can only be determined by after-the-fact measurements, comparison with unpublished data and *a priori* reconstruction using nannoplankton-environment relationship models to obtain predictable ecological patterns. We report here the results of a study, the first step in the reconstruction of nannoplankton populations at the time of the spill. We began monthly sampling in January 2011, along three transects across the shelf of the Florida Panhandle. We have taken about 2000 samples through the photic zone via Niskin-bottle rosettes which also provide water-chemistry and chlorophyll data. Quantitative nannoplankton census data are taken via scanning electron microscopy. Our nannofossil results to date indicate that unfortunately, samples taken a year after the spill do not represent floras at the time of the spill because of the 100-year Mississippi flood event that placed a thick lens of fresh water over our study

area. In addition, De Soto Canyon provides another variable since it can funnel open GOM waters high up onto the shelves in the Florida Panhandle region so that near-shore nannoplankton assemblages there can at times mimic those of the open ocean. The synthesis so far of the data sets from three different segments of the year (four-months each) indicate that there has been too much seasonal and inter-annual variation in nannoplankton populations to allow a predictable pattern to emerge at the present time, hence, more sampling will be required to achieve an *a priori* reconstruction.

Deepwater Horizon Impacts on the Pelagic Foodweb: Stable Isotope Constraints on Zooplankton Carbon and Nitrogen Sources

D. A. O. Lee-Patterson, S. C. Weber, A. Fernandez, J. P. Montoya
Georgia Institute of Technology, Atlanta, GA

The offshore ecosystem of the Northern Gulf of Mexico is affected by inputs of oil and gas from natural seeps as well as accidental releases, such as the Deepwater Horizon (DWH) incident in 2010, which discharged an unprecedented volume of oil and gas into pelagic waters. We collected zooplankton from the Northern Gulf one month after the DWH wellhead was sealed, and have resampled the system annually. We use stable isotope measurements (δ13C and δ15N) to quantify the incorporation of low δ13C petrocarbon and low δ15N material from nitrogen fixation into the marine food web. Immediately after the spill, we found low δ13C values, particularly in the small size fraction of animals collected during the day in the mixed layer, and a shift to higher δ13C values at night. Small zooplankton from the mixed layer also showed diel shifts in δ15N, with low values predominating during the day and higher values at night. These diel changes reflect the integration of petrocarbon and recently fixed nitrogen fixation into the pelagic foodweb, and imply that incorporation of both petrocarbon and recently fixed nitrogen occurred primarily in the mixed layer. Zooplankton collected in subsequent years do not show consistent diel shifts in δ13C, though surface δ15N values were generally lower during the day than at night. Our data imply that the DWH spill made a measurable contribution to zooplankton production, and that this direct impact was relatively short-lived.

Oil Spills, Adaptation, and Gene Flow: Genomic Insights for Fisheries Management in Impacted Systems

D. S. Portnoy, J. R. Gold
Texas A&M University - Corpus Christi, Corpus Christi, TX

Genetic approaches have played an important role in the management of fisheries resources by providing methods to identify population (stock) boundaries, quantify connectivity between populations, and estimate genetic demographic parameters. Recent analytical and technological advances have increased the quantity and quality of molecular data accessible, while decreasing associated costs and time. It is now possible to accurately assay thousands to tens of thousands of genetic markers spread evenly throughout a genome. These assays offer increased power for detecting population structure and connectivity, but more importantly provide the opportunity to detect candidate genes or chromosomal regions involved in adaptation on local scales. For species impacted by sudden and intense environmental disturbances, these technological advances can be used to compare genomic variation before and after an environmental disturbance in order to assess possible adaptive responses and better understand resilience. Continued genomic monitoring of recovering populations also may provide data on the extent and nature of the recovery. Current work in the Marine Genomics

Laboratory at the Harte Research Institute at Texas A&M University - Corpus Christi revolves around using these new approaches on several species of fishes, including sharks.

Temporal and Spatial Variation in the Carbon and Nitrogen Isotope Ratios of Mesozooplankton in the Central Gulf of Mexico

S. Z. Herzka[1], J. C. Herguera[1], D. López Veneroni[2]
[1]Center for Scientific Research and Higher Education of Ensenada (CICESE), Ensenada, Mexico, [2]Instituto Mexicano del Petróleo, Distrito Federal, Mexico

The isotopic composition (δ13C, δ15N) of pelagic mesozooplankton (> 333 µm) has been used to infer sources of primary production, discriminate between upwelled and fixed nitrogen and as a proxy for the isotopic composition of the base of the food web. Within the context of the GM oil spill, δ13C ratios traced the incorporation of petroleum-based hydrocarbons into the marine food web. We analyzed the isotopic composition of copepods and euphausiids caught in surface waters (< 200 m) throughout Mexico's deepwater region (depths > 1000 m). Up to 44 sampling stations were covered in November 2010 (fall), July 2011 (summer) and February 2013 (winter). Mean δ13C values of copepods and euphausiids were similar during the fall and summer (-21.6 to -20.7‰) and exhibited limited spatial variation (< 2 ‰). However, those caught in winter were ca. 1‰ lighter. δ13C values were consistent with phytoplankton as the dominant carbon source, although terrestrial C-3 organic matter may contribute close to the platform. Mean δ15N values of each taxa were variable and did not differ significantly between cruises (range 1.5 to 7.3‰), suggesting spatial variation in nitrogen sources and taxon-specific differences in trophic level. The presence of light δ15N values in the central GM (< 4‰) is consistent with previous reports highlighting the importance of nitrogen fixation in oligotrophic waters. Euphausiids were significantly enriched in 15N relative to copepods. Considering an approximate trophic enrichment of 3.5‰, this is consistent with the higher trophic level of euphausiids. Our results support the value of using the isotopic composition of pelagic mesozooplankton as indicators of carbon and nitrogen sources over broad spatial scales.

Age-based Batch Fecundity in Red Snapper Before and After the Deepwater Horizon Oil Spill of 2010

D. Flawd, D. Murie, D. Parkyn
University of Florida, Gainesville, FL

The red snapper (*Lutjanus campechanus*) is in the midst of a fisheries management rebuilding plan due to population declines. As a commercially and recreationally important species, assessing effects from the Deepwater Horizon oil spill of 2010 is critical, specifically on reproductive biology. Batch fecundity, the number of eggs released during a single spawning event within the spawning season, will be estimated in red snapper from Louisiana and West Florida before (1991-2004, 2005-2009) and after (2010-2014) the oil spill that occurred in the summer of 2010. Batch fecundity will be compared between both regions and time periods using a multivariate analysis of variance, including variables such as year, month, and female length, weight, age, and gonad weight. Furthermore, batch fecundity will be compared among age classes between the two regions and time periods to determine any age-specific effects, which will be modeled using logistic regression and include an AIC analysis for best fit. Any differences in batch fecundity of red snapper from Louisiana before and after 2010, relative to the Florida reference area, would need to be incorporated into stock assessments for rebuilding plans.

Temporal Variations in the Vertical Distribution of Deep-water Scattering Layers in the Gulf of Mexico

K. M. Boswell[1], M. A. D'Elia[1], J. D. Warren[2], T. T. Sutton[3]
[1]FIU, North Miami, FL, [2]Stony Brook University, Southampton, NY, [3]Nova Southeastern University, Dania Beach, FL

Sound scattering layers (SSLs) are ubiquitous throughout the world's oceans and the organisms comprising these layers are important components of these vast ecosystems. The depths at which SSLs occur is dynamic and is often dependent on the depth of the water column and time of day, which gives rise to well-recognized and remarkable diel vertical migration (DVM) patterns. This dramatic vertical movement between biomes offers opportunities for intense ecological interactions between SSLs and surface oriented communities including predator-prey relationships and energy transfer. Understanding how the community structure within SSLs varies will help to better characterize the important ecological role these organisms play. Using continuous hydroacoustic data collected in the northern Gulf of Mexico, we developed methods to partition the SSL acoustic biomass detected at 18 and 38 kHz into broad taxonomic categories. Results indicate that SSL DVM is an intricate process. We detected a well-defined DVM to depths of 1000 m which featured complex patterns during crepuscular periods and large shifts in both vertical position and the taxonomic character of the SSLs.

Baseline Information for Fish Growth Rates and Microchemistry Obtained from Pre-Columbian Fish Otoliths

B. C. Houston[1], E. A. Southard[2], D. L. Jones[1], E. B. Peebles[1]
[1]University of South Florida, St. Petersburg, FL, [2]University of South Florida, Tampa, FL

The absence of baseline information prior to the Deepwater Horizon oil spill is often cited as an impediment to assessing the spill's impacts. We present data from a pre-industrial-age baseline to compare fish growth rates between ancient and modern times. Fish growth rates have a strong potential to predict individual fitness, overall population health, and equate to changes in survival and lifetime reproductive potential. We sampled fish otoliths from three sources to compare growth rates: 1) ancient fish otoliths from Native American middens in west-central Florida, 2) modern otoliths from west-central Florida, and 3) modern otoliths collected from coastal Louisiana immediately following the Deepwater Horizon spill. We are also using laser-ablation ICP-MS to compare the microchemistry of 25 elemental analytes among the three otolith sources. Initial findings based on red drum have identified significant variations in growth rate among these sources. Microchemical analyses are ongoing.

Photo-enhanced Toxicity of Fresh and Weathered Macondo Crude Oils to Marine Organisms under Natural and Artificial Sunlight

B. E. Finch, W. A. Stubblefield
Oregon State University, Albany, OR

Crude oils contain a mixture of hydrocarbons including phototoxic polycyclic aromatic hydrocarbons (PAHs) that are novel in their ability to absorb and respond to ultraviolet (UV) light. PAH absorption of UV light can substantially increase toxicity to marine organisms. The objective of the current study was to examine the potential for photo-enhanced toxicity of fresh and naturally weathered Macondo (MC-

252) crude oils collected from the Deepwater Horizon incident to mysid shrimp, inland silverside, sheepshead minnow, and Gulf killifish. Acute toxicity tests were conducted using combinations of natural or artificial sunlight and low energy water-accommodated fractions (LEWAFs) of fresh and weathered MC-252 crude oils. LEWAFs were prepared with crude oil alone as well as in combination with the dispersant Corexit 9500. Validation studies were conducted to compare toxicity observed over one diurnal period under artificial and natural UV light conditions. Comparisons between different crude oils and species sensitivity were made using median lethal LEWAF concentrations (LC50s). Data demonstrated MC-252 fresh crude oil was slightly more toxic than weathered crude oils, both in the presence and absence of UV light. The addition of Corexit 9500 to crude oil increased toxicity compared to tests with crude oil alone, by increasing phototoxic PAH concentrations in LEWAFs.

Biomarkers of Exposure to Polycyclic Aromatic Hydrocarbons in Gulf of Mexico Reef Fishes

M. O. James[1], M. Smeltz[1], C. Ghiran[1], J. H. Tarnecki[2], W. H. Patterson[2]
[1]University of Florida, Gainesville, FL, [2]University of South Alabama, Dauphin Island, AL

As part of a survey to determine the possible exposure of reef fish in the Gulf of Mexico to polycyclic aromatic hydrocarbons (PAH) that can form following an oil spill, we investigated hepatic biomarkers of exposure in post-mitochondrial supernatant fractions from four species of reef fish captured in the Gulf of Mexico between 2011 and 2014. The fish studied were the red snapper, vermillion snapper, red porgy and gray triggerfish. The biomarkers were ethoxyresorufin O-deethylase (EROD), glutathione transferase (GST) and glutathione peroxidase (GPx). GST and GPx activities were lower in the vermillion snapper than other species, which were similar to one-another. Throughout the period studied, average EROD activity was approximately seven-fold higher in gray triggerfish than red snapper and five-fold higher than vermillion snapper. Red porgy exhibited a greater variability of EROD activity than the other species, however the mean activity was lower than gray triggerfish. We observed that the gray triggerfish had fatty livers and the fat separated upon preparation of the post-mitochondrial supernatants. Heptane extracts of this fat contained fluorescent material with properties similar to polycylic aromatic hydrocarbons (excitation 360 nm emission 475 nm). Separation of the fat extracts by reverse-phase HPLC revealed a pattern of four fluorescent peaks: the amount of one of these peaks showed a positive correlation with EROD activity in that sample. The origin and nature of this peak is under investigation. This research demonstrated that biomarkers of exposure to PAH vary considerably between species and may depend on the fish biology as well as exposure history.

Isotopic Comparison of the Eye Lens with Other Tissues in Golden Tilefish: New Proxies for Site Fidelity and Trophic Position of Oil Exposed Fish

J. L. Fenton, E. B. Peebles, D. J. Hollander
University of South Florida, St. Petersburg, FL

Conservative isotopic records within fish eye lenses are being evaluated as records of trophic position and geographic history, both of which are relevant to understanding fish exposure to oil spills. However, the temporal duration and temporal concurrence represented by the outermost layer of the hardened, cortical portion of the eye lens (“outer lens”) is not yet known. We compared the δ13C and δ15N of the outer lens of 36 Golden Tilefish with δ13C and δ15N from six tissue types that have intermediate tissue turnover rates (muscle, liver, heart, brain, spleen, and blood), and used reduced-major-axis regression to

quantify the isotopic agreement between the outer lens and the six other tissues. This quantification included metrics for trueness, precision, and temporal concurrence. Isotopes in nearly all pairwise tissue comparisons were significantly correlated, except for those involving liver δ13C of either the outer lens or the other five tissue types. Liver had higher C:N than other tissues types, and it is thus suspected that this lack of correlation may have been due to isotopic interference from storage lipids. Muscle, which has a turnover rate measured in months, had the most accurate isotopic relationship (high trueness and high precision) with the outer lens, indicating that the outer lens also represents a temporal period measured in months.

Microbial Community Response to Natural Organic Matter Enrichments After Being Primed by Deepwater Horizon Oiling

S. Beeler, A. T. Paterson, **A. S. Engel**
University of Tennessee-Knoxville, Knoxville, TN

Coastal marshes have the potential to accumulate large quantities of organic matter (OM), as long as burial is faster than turnover by the soil microbial communities. Changes to degradation rates are possible when specific communities are primed ecologically by exogenous OM, such as oil. Consequently, microbial communities primed by oil may breakdown natural marsh OM more rapidly, and thereby change OM turnover rates. To evaluate community-level response from the input of fresh OM, after being oiled, natural OM degradation rates were experimentally determined with native soil from two Louisiana marshes that had differing oiling histories. *Spartina alterniflora* leachate produced by tyndallisation was added to the soil to represent fresh natural OM. The fastest degradation rates were observed from more heavily oiled soils. Leachate-amended soil communities significantly differed from controls (with no leachate added). Relative abundances of Clostridia and Fusobacteria, as well as proteobacterial groups Xanthomonadales, Desulfovibrionales, Rhodospirilales, and Mariprofundales, increased from soil with the highest degradation rates. These microbial taxa are found in native marsh soils now, at differing population abundances than before the oil spill. Consequently, evaluating microbial communities from marshes over time, as part of longitudinal studies since the DWH oil spill, may be complicated if there are lasting effects of priming on the microbial community compositions.

Dynamics of Demersal Fish Communities on the Northern Gulf of Mexico Continental Shelf

S. A. Murawski, E. B. Peebles
University of South Florida, St. Petersburg, FL

Monitoring of demersal fish populations in the northern Gulf of Mexico is accomplished using a variety of fishery-independent sampling programs conducted by state and federal agencies and academic institutions. Communities of demersal fishes in the region are structured primarily by depth and bottom type. Changes in these communities are driven by environmental variation and human-use impacts. We interpret the stability of such communities and variability over time using multivariate techniques (e.g., canonical correlation analysis, multi-dimensional scaling, and time series analysis) applied to data from trawl, longline and ichthyoplankton surveys. Results are interpreted with respect to the time series of data spanning and collected subsequent to the Deepwater Horizon oil spill.

Spatial and Temporal Effects of the Deepwater Horizon Oil Spill on Estuarine Fish Growth in the Gulf of Mexico

D. J. Murie, D. C. Parkyn
University of Florida, Fisheries & Aquatic Sciences, Gainesville, FL

One of the most immediate concerns for fisheries in the Gulf of Mexico following the Deepwater Horizon (DWH) oil spill in April 2010 was to what extent recreational and commercial fisheries would be impacted. Changes in the productivity of fish species can have profound ecological and economic consequences. Small changes in the growth and therefore size of fish can ultimately lead to large changes in productivity of stocks. The complete growth history of a fish, from its birth to capture, is recorded in its otoliths or "ear stones", which show annual growth increments. One specific goal of our ongoing research is to focus on the spatial and temporal effects of the DWH oil spill on the growth and productivity of potentially-impacted estuarine fishes, such as spotted seatrout and red drum. To do this, growth patterns captured in their otoliths just prior to and after the spill event are measured on an age-specific basis for fish collected both in Louisiana (area impacted by oil) and the west coast of Florida; the latter acting as a "reference" or relatively non-impacted area. Biologically relevant differences in growth will be incorporated into age-structured stock assessments to detect changes in productivity of these important coastal fish stocks in the Gulf of Mexico.

Monitoring Benthic Habitats within Mississippi Sound Using High Precision Multibeam Sonar

I. Church
University of Southern Mississippi, Stennis Space Center, MS

Mississippi Sound contains sensitive benthic habitats, many of which are of local economic interest. Maintaining the success of these habitats is dependent on a balance of external environmental factors. In an effort to understand future changes in habitat sustainability from environmental imbalances and potential toxicant exposure, a comprehensive acoustic benthic monitoring campaign of select areas within Mississippi Sound is being investigated. Repetitive acoustic backscatter and bathymetry mapping of key benthic habitats at regular time intervals allows for the natural dynamics of the environment to be observed along with any anomalies. The technical challenge of a monitoring program using three-dimensional acoustics is to determine the actual level of detectable change. Though development of innovative approaches to data collection at multiple acoustic frequencies, data processing, and high precision system integration, the level of confidence in detectible change can be increased and more meaningful results can be obtained from the monitoring program. The goal of this project is to detect small changes in the benthic environment and to correlate that observed change to external environmental factors. This will lead to an improved understanding of the habitat's dependence on certain conditions, their resiliency in the face of natural dynamics, and the impact of external forces.

Potential Oil Spill Effects on Behavior and Group Size of Common Bottlenose Dolphins (*Tursiops truncatus*) in Galveston Ship Channel

E. Mattson[1], D. Orbach[2], S. Piwetz[2], B. Würsig[2], W. Highfield[2], C. Marshall[2]
[1]Department of Marine Biology, Texas A&M University at Galveston, Galveston, TX, [2]Texas A&M University at Galveston, Galveston, TX

Oil spills can be intense anthropogenic stressors for marine mammals. Common bottlenose dolphins, *Tursiops truncatus*, are susceptible to health complications from both oil ingestion and the inhalation of toxic fumes from oil slicks. Bottlenose dolphins try to avoid thicker oils, but have difficulty avoiding thinner, lighter-sheen oils. Previous reports on the behavioral responses of dolphins to oil spills were in direct reaction to the spills and failed to provide the baseline data necessary to detect change. We report changes in group size, behavior (resting, foraging, traveling, socializing), and distribution of bottlenose dolphins in the Galveston Ship Channel before and after the Kirby Barge oil spill. This oil spill on 22 March 2014, leaked an estimated 168,000 gallons of thick bunker fuel oil into Galveston Bay. Data on bottlenose dolphins were collected intermittently by opportunistic boat-based observations from October 2011 to October 2014. Dolphins left the area for at least three days immediately following the spill, but began to return on March 26th. Group size did not vary significantly between the summer seasons across years or between the spring of the spill and the following summer (Kruskal-Wallis: p-value>0.9). However, resting and socializing behaviors varied significantly between all summer data and the spring oil spill data (X^2=9.95, df=1, p-value<0.01), with more socializing in the spring months directly following the spill than in comparable summer periods (z=2.82). It is not clear what role seasonal variations played in these behavioral differences. Potential behavioral responses to the spill did not appear overtly negative or prolonged. The detected behavioral variation reinforces the importance of implementing baseline data collection to better understand the short-term effects of oil spills on dolphin behavior, as well as to improve oil spill response efforts and management strategies.

Parasite Component Community of *Fundulus grandis* as an Indicator of Acute and Chronic Environmental Effects of the 2010 BP Deepwater Horizon Oil Spill in Barataria Bay, Louisiana

S. A. Bullard[1], **C. F. Ruiz**[2]
[1]School of Fisheries, Auburn University, Auburn, AL, [2]Texas A&M University, Galveston, TX

Fish parasites comprise a large portion of marine biodiversity but so far have been underutilized as Gulf of Mexico bioindicators. Shifts in parasite diversity, prevalence, and intensity resulting from the DHOS could indicate spill-related changes to water quality, abundances and immunological health of free-living organisms, or the food web. Ectoparasites with direct life cycles may be sentinels for acute spill effects, as they are typically small, have high surface area to volume ratios, and remain immersed in seawater. Endoparasites with indirect life cycles involving food-web mediated transmission may be sentinels for detecting chronic spill effects, as they reside in a host where they are less vulnerable to toxins and have larvae requiring predator/prey transmission. As such, environmental perturbations or toxicological events affecting food-web structure may impact endoparasites more than ectoparasites. Four reference sites and 4 oiled sites were sampled continuously for 12 months within Barataria Bay, accounting for natural seasonal variation in parasite abundance and intensity. The parasite component community of *F. grandis* documented from Barataria Bay consisted of 44 species (31 endoparasites; 13 ectoparasites) that infected 23 fish tissues. Of these parasite species, 10 are putatively new to science and are not

presently named in the primary literature, 24 constitute new host records to *F. grandis*, and nearly all, 42 of 44 (95%), are putatively new locality records for the north-western Gulf of Mexico. Prevalence of acanthocephalans (21.4% in non-oiled sites vs. 3.2% in oiled sites), copepods (20.5% vs. 33.6%), and branchiurans (13.6% vs. 27.3%) were detected. Digenean metacercariae infecting gill and heart, monogenoideans infecting skin, and nematodes infecting body cavity each have a significantly higher log mean intensity in oiled sites. Seasonal effects were statistically detected in myxozoans and digeneans, and those seasonal patterns were not significantly different between oiled and non-oiled sites. This work was supported by grants from the AL MESC, GoMRI, and NSF.

Putative Eye Abnormalities in Atlantic Midshipman, *Porichthys plectrodon* (Batrachoidiformes: Batrachoididae) from the North-Central Gulf of Mexico off Louisiana

S. A. Bullard[1], M. R. Womble[2]
[1]School of Fisheries, Auburn University, Auburn, AL, [2]Auburn University, Auburn, AL

Ocular deformities in adult fish, especially wild-caught marine fish, are seldom reported but perhaps not as rare as the literature might suggest. While conducting biological collections in the north-central Gulf of Mexico off Louisiana we collected several Atlantic midshipmen that exhibited eye abnormalities. Specimens were immediately preserved in 10% neutral buffered formalin and subsequently photographed in the laboratory before performing whole-body clearing/staining and routine histopathology. Seemingly normal, conspecific specimens were sourced from fisheries independent trawl surveys conducted by the NOAA National Marine Fisheries Service during Fall 2012 and previous years in the eastern Gulf of Mexico off Florida and processed in parallel for comparative purposes. Grossly, in abnormal specimens the eyestalk was reduced, the eye faced laterad, the skin covering the globe was thickened, in some specimens the globe was apparently absent and appeared to lack a lens, and the pigment adjacent to the eye was in disarray. Osteologically, in abnormal specimens the globe was positioned at midline of the syncranium (not elevated above the level of the premaxilla or above the lateral edge of neurocranium) and the eye was directed laterally, not dorsally. Histologically, all specimens, surprisingly, had all of the key tissues and structures comprising the fish eye. However, abnormal specimens presented macroscopic changes associated with the eyestalk and globe along with corresponding histological changes, including a markedly thickened and uneven cornea, thickened sclera, and elaboration of the choroid rete between the cornea and sclera. Although only based on a single collection of fish at a single time point, the results of the present study encourage additional investigations on the presence and etiology of abnormalities in fishes of the continental shelf off Louisiana, Mississippi, and Alabama; where much recent attention has been cast on fish diseases following the DHOS.

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

Initial Investigations of the Microbial Ecology of Tar Balls and Their Impact on Anaerobic Respiratory Activity

J**. M. Johnson[1]**, B. H. Harriman[1], C. Aeppli[2], E. Aydin[1], V. Bonifay[1], J. M. Suflita[1], J. Sunner[1], A. V. Callaghan[1]
[1]University of Oklahoma, Norman, OK, [2]Bigelow Laboratory for Ocean Sciences, Boothbay, ME

Weathering of the spilt DWH crude oil results in the formation of tar balls that deposit on Gulf Coast beaches. The microbial ecology of tar balls and their potential impact on coastal ecosystems are not well characterized. Tar balls were collected from the beaches of Gulf Shores and Fort Morgan, Alabama and used for metagenomic sequencing and to test their impact on anaerobic respiratory activity as a prelude to biodegradation experiments. Using $^{35}SO_4^{2-}$ as a tracer, seawater was found to readily penetrate tar balls. An assessment of ^{35}S-sulfate reduction assays in sand/seawater incubations amended with homogenized tar balls (0 to 100 % w/w) revealed that tar balls would not impact the endogenous rates of microbial respiration. In some incubations, a slight stimulation in sulfate reduction was evident. Metagenomic profiling of tar balls via Illumina MiSeq revealed that there are significant phylogenetic differences in the tar balls collected between the two beach sites. Evidence of the genetic potential for both aerobic and anaerobic hydrocarbon biodegradation was supported by the detection of alkane hydroxylase (*alkB*), naphthylmethylsuccinate, alkylsuccinate, and benzylsuccinate synthase genes (*nmsA*, *assA*, and *bssA*). Collectively, these findings suggest that tar balls are permeable, not toxic to microorganisms, and may be subject to further biotransformation processes by indigenous microbial communities.

A Spatial and Temporal Investigation of Carbon Isotopes in POC in the Gulf of Mexico

K. Rogers[1], J. Montoya[2], S. Weber[2], J. Chanton[1]
[1]Florida State University, Tallahassee, FL, [2]Georgia Institute of Technology, Atlanta, GA

The Deepwater Horizon blowout released 500,000t of gaseous hydrocarbon into the water column, but <0.01% of this reached the sea surface. Metabolically efficient methanotrophs consumed the gasses, converting them into biomass that was then consumed by other organisms. By analyzing POC samples, carbon isotopes can trace the original gas up the food chain. POC samples were collected from Desoto Canyon and other seep sites across the Northern GOM. Seawater was filtered, collecting the POC on glass microfiber filters, which were then acid fumed, dried and analyzed for δ13C and Δ14C. Preliminary trends in the data show more depleted δ13C signatures at greater depths in the water column. These depleted δ13C samples also have highly depleted Δ14C values.

Single-cell Genomics Reveals Features of Uncultured, Indigenous Deep-sea Bacteria that Dominated the DWH Plume and Contaminated Surface Sediments

O. Mason
Florida State University, Tallahassee, FL

One theme that emerged from the collective work describing the microbial community response to hydrocarbons input during the DWH oil spill was the temporal succession of indigenous deep-sea Proteobacteria. In particular, Oceanospirillales and Colwellia dominated the deep-sea plume at different times during the spill. Colwellia was also abundant in surface sediments contaminated during the spill. Both of these dominant species eluded cultivation efforts, thus their physiology remained enigmatic. Using single-cell genomics Oceanospirillales and Colwellia cells were isolated from the deep-sea DWH plume and their genomes were sequenced. Genome annotation revealed several common features, for example, genes coding for chemotaxis and motility, and nutrient acquisition strategies. Several differences emerged, namely the dominant hydrocarbon degradation pathways, iron acquisition strategies, and respiration capabilities. Oceanospirillales appears to be capable of cyclohexane degradation, while Colwellia may be able to oxidize gaseous and aromatic hydrocarbons, although its role in hydrocarbon degradation requires further research. Unlike Oceanospirillales, Colwellia encoded a pathway for denitrification. Last, Oceanospirillales had genes coding for siderophore production, while Colwellia appeared to lack these genes. The genome features of the uncultured, resident deep-sea Proteobacteria that dominated the DWH plume and surface sediments provided important information that could be used as a predictive tool regarding mitigating ecosystem services provided by indigenous microorganisms during an oil spill.

A Quantitative Measure of the Hydrocarbon Consumption Rate Using *Alcanivorax borkumensis*

L. D. Bookstaver[1], M. Bookstaver[1], A. Bose[2], A. Tripathi[1]
[1]Brown University, Providence, RI, [2]University of Rhode Island, Kingston, RI

Alcanivorax borkumensis is commonly known for its role as a marine bacterium that degrades hydrocarbons present on the surface of water after the occurrence of oil spills. Insoluble hydrocarbons are released into the water as a result of a deep-water oil spill and reside on the surface of the water. Previous studies have shown that *Alcanivorax borkumensis* is one of the main bacteria responsible for degrading the hydrocarbons on the surface, but not much is known about its consumption rate of the oil. Here, we use an innovative design to measure the oil consumption rate by *Alcanivorax borkumensis*. We grow *Alcanivorax borkumensis* to different points on the growth curve and examine the consumption of the oil in relation to where on the growth curve the bacteria are grown to. We probe the consumption rates for different carbon sources, such as dissolved organic carbon, alkanes, and branched alkanes. We use these results to document the patterns and variability in hydrocarbon rates of consumption. This study can help in our understanding of how to best aid marine bacterium, like *Alcanivorax borkumensis*, in the bioremediation of oil spills.

Unraveling Microbial Degradation of Dispersant and Water-Soluble Oil Compounds in Deep Seawater from the Gulf of Mexico using Ultrahigh Resolution Mass Spectrometry

M. Seidel[1,2], S. Kleindienst[1], L. Babcock-Adams[1], T. Dittmar[2], S. B. Joye[1], P. M. Medeiros[1]
[1]University of Georgia (Department of Marine Sciences), Athens, GA, [2]University of Oldenburg (ICBM-MPI Bridging Group), Oldenburg, Germany

Nearly three million liters of chemical dispersants (Corexit 9500 and 9527) were applied directly to the wellhead at a water depth of ca. 1500 m during the 2010 Deepwater Horizon oil spill in the Gulf of Mexico (GoM). Such a large-scale application of dispersants in the deep ocean is unprecedented, especially considering that the influence of dispersants on oil biodegradation has not been completely constrained yet. Here, we report results from microcosm studies using GoM deep seawater which was amended with either dispersant, oil, dispersed oil or dispersed oil and nutrients. Ultrahigh resolution mass spectrometry was used to discern the microbial degradation of water-soluble oil and dispersant-derived organic compounds at the molecular level. We found that the addition of the dispersant Corexit enhanced the microbial processing of sulfur-containing compounds in the setups with the dispersed oil, while nitrogen-bearing compounds were preferentially degraded in the oil-only setups. Our results, therefore, suggest that dispersants may have a significant effect on the preferential biodegradation of oil-derived compounds in deep sea spills.

Interpretation of Oxygen Profiles in the Aftermath of the BP/Deepwater Horizon Hydrocarbon Discharge

C. Meile[1], M. Lai[1], A. Bracco[2], H. Luo[2], S. Joye[1]
[1]University of Georgia, Athens, GA, [2]Georgia Institute of Technology, Atlanta, GA

In the aftermath of the BP/Deepwater Horizon hydrocarbon discharge in 2010, a subsurface plume characterized by hydrocarbon concentrations highly elevated above background and a drawdown of O2 was documented in Gulf of Mexico deep water to the southwest of the wellhead. The magnitude of the O2 deficit and the processes responsible were poorly constrained and remain a subject of debate. Here, we present an analysis of O2 drawdown from two research cruises conducted near and to the southwest of the wellhead and introduce a novel interpolation method to quantify total O2 consumption. We illustrate that accurate estimates of total O2 depletion must account for water movement and, more importantly, must capture the spatial structure of the O2 anomaly field, which is difficult with the sparse sampling regime typically utilized on oceanographic cruises. We further show that in late May/early June in the vicinity of the wellhead, increased oxygen anomalies correlate with increasing methane oxidation rates and distance from the wellhead, which reflects the exposure time of the microbial community to hydrocarbons.

Bioremediation of Crude Oil by Indigenous Bacteria

X. Hu, H. Wang
Yantai Institute of Coastal Zone Research Chinese Academy of Sciences, Yantai, CHINA

Increasing exploitation, production, transportation and storage of crude oil industry have led to more accidentally spilled contaminants. Several techniques, including physical, chemical, and biological

methods, are used to recover spilled oil from the environment. Bioremediation, mainly by indigenous bacteria, has been regarded as a cost-effective green alternative to clean up oil pollution after an oil spill. Moreover, the recent omics revolution has led to leaps in our understanding of microbial communities, and some of the conditions that promote predictable activity in contaminated sites and heterogeneous environments. Combinations of omics tools and new bioinformatics approaches allow us to understand integrated activity patterns between oil pollutants and microorganisms, and determine how this metaorganism can be modified to maximize growth, appropriate assembly of microbial communities, and, ultimately, bioremediation activity. In our laboratory, we have conducted omics-mediated experiments to discover the bacterial communities and the mechanisms during bioremediation. Our results revealed that (1) nutrient amendment could significantly improve the efficiency of oil-biodegradation; (2) the bacterial community structure showed dramatic changes during the bioremediation process; (3) the immobilization technique could increase the efficiency of hydrocarbon degradation; (4) the omics strategies could clarify and confirm the hydrocarbon degradation pathways. The insights and theories of our study will increase the understanding of the hydrocarbon degradation process and provide fundamental evidences for in situ bioremediation of crude oil spills.

Unraveling Who Is Who in Methanogenic Oil Degradation

A. J. Cavaleiro[1], A. F. Salvador[1], J. I. Alves[1], A. A. M. Langenhoff[2,1], A. J. M. Stams[3,1], M. M. Alves[1], D. Z. Sousa[3,1]

[1]Centre of Biological Engineering, University of Minho, Braga, Portugal, [2]Sub-department of Environmental Technology, Wageningen University, Wageningen, Netherlands, [3]Laboratory of Microbiology, Wageningen University, Wageningen, Netherlands

Methanogenesis from hydrocarbons is a potentially important component of attenuation in water and sediments impacted by oil spills. The largest fraction of crude oil consists of aliphatic hydrocarbons (AHC). Current knowledge on key microorganisms degrading alkenes is scarce and is a central question addressed in our research. A methanogenic hexadecene (Hxd)-degrading consortium was obtained from laboratory microcosms inoculated with anaerobic granular sludge, and characterized by 16S rRNA gene amplification, cloning and sequencing. We have learned by community analysis that the present bacteria belong mainly to Syntrophaceae and Synergistaceae families. A Syntrophus-like microorganism (96% similarity at genera level) is possibly involved in Hxd degradation. Known methanogens utilizing acetate and H2/CO2 were identified, namely Methanosaeta-, Methanobacterium- and Methanolinea-related microorganisms, and were likely the syntrophic partners in Hxd degradation. With these results we find hints for similar pathways involved in alkenes and alkanes biodegradation. For alkanes, complete degradation to methane can occur through syntrophic interactions between bacteria and methanogens. This is the first time that an alkene-degrading methanogenic mixed community is characterized. Novel microorganisms involved in AHC degradation could be identified. This information is useful for understanding “who is doing what”, and at what rate. It can be used for innovative biotechnological solutions for deep contaminated sites clean-up.

Biodegradation of Dispersed versus Non-Dispersed Oil by Surface Microbial Communities

S. J. Harrison, S. Y. Malkin, K. M. Loftis, S. B. Joye
University of Georgia, Athens, GA

Following the Deepwater Horizon oil spill, approximately 5.3 million liters of chemical dispersants, Corexit 9500 and Corexit 9527, were applied to surface oil slicks in the Gulf of Mexico. Although chemical dispersants are designed to disperse surface oil slicks in order to promote biodegradation, little is known about how chemical dispersants and chemically dispersed oil impact the structure of surface microbial communities or about how signature of the oil itself evolves during microbial biodegradation in the presence of dispersants. Understanding how microbial communities respond to dispersants and dispersed oil and what becomes of the dispersed oil is critical to evaluating the effectiveness of dispersant application. In this study, indigenous surface water bacterial communities surrounding a natural oil slick from the Gulf of Mexico were incubated in 1L microcosms at surface temperatures for 24 days. Microcosms were amended with the water accommodated fraction (WAF) of dispersed and non-dispersed oil, with and without nutrients, and sacrificed at 0, 7, 14, and 24 days (n=3). The nonpolar extract of microcosm water samples was characterized using GC-MS and 2D GC-MS and compared to the parent crude oil. Dispersants had clear, yet unanticipated impacts on the chemical composition of oil and on oil biodegradation rates.

Environmental Conditions Are Key to Controlling the Development of Oil Degraders in the Gulf of Mexico Waters

Z. Liu, J. Liu, H. Bacosa, D. Erdner
The University of Texas at Austin, Port Aransas, TX

The development of oil-degrading bacterial community in oil-contaminated marine waters depends on many environmental factors, such as solar irradiance, temperature, nutrients and initial bacterial community, yet their respective roles have not been systematically studied. This knowledge is critical to evaluate the fate of oil, as oil spills, such as the Deepwater Horizon (DWH) one, are often across large environmental gradients in marine waters. From both field work and laboratory incubations, we systematically examined the role of environment conditions in controlling the evolvement of bacterial community structure. Our data showed that *Erythrobacter*, *Rhodovulum*, *Stappia* and *Thalassospira* of Alphaproteobacteria and *Alteromonas* and *Marinobacter* of Gammaproteobacteria were the prevailing groups in the sea surface oil mousses, which may relate to high temperatures and strong irradiance in surface Gulf waters. Our later on-deck incubations confirmed that sunlight selected degraders such as *Alteromonas*, *Marinobacteria*, *Halomonas*, *Labrenzia*, *Bartonella*, and *Sandarakinotalea*, while dark conditions selected *Alcanivorax*, *Pseudomonas*, *Winogradkyella*, *Erythrobacter Rhodovulum*, *Coxiella*, *Nautella*, and *Stappia*. Temperature also has a profound effect on the oil-degrading community, as *Cycloclasticus*, *Alcanivorax*, *Phaeobacter*, *Cobetia*, *Pseudoalteromonas*, *Reinekea* and *Alteromonas* developed well at 4°C, while *Winogradskyella*, *Oleibacter*, *Roseovarius*, *Thalassobius*, *Bacteriovorax*, *Thalassospira*, *Hyphomonas*, *Erythrobacter* and *Oceanobacter* at 24°C. This presentation will synthesize the development of oil-degrading bacteria communities impacted by light, temperature and initial bacterial communities.

Intact Ribosomal RNA in Mercury-Poisoned Sediment Trap Samples: Preservation or Growth?

B. J. MacGregor[1], K. Ziervogel[1], U. Passow[2]
[1]University of North Carolina, Chapel Hill, NC, [2]University of California at Santa Barbara, Santa Barbara, CA

Mercuric chloride ($HgCl_2$) is a common preservative in sediment traps, broadly reactive with biomolecules and fatal at low concentrations. Ribosomal RNA (rRNA) is considered an indicator of currently active microbes; susceptibility to chemical and enzymatic degradation makes it unlikely to persist once cells die. Surprisingly, high rRNA concentrations were found in $HgCl_2$-preserved sediment trap samples after a one-year deployment near the sunken Deepwater Horizon wellhead. We are therefore investigating the long-term effects of $HgCl_2$ on pure-culture and particle-associated microbes. With pure-culture Escherichia coli in artificial seawater plus $HgCl_2$, high concentrations of apparently intact rRNA were recovered even after 80 days at 4°C, although no colony-forming bacteria remained. Degradation was faster at ~21°C, but still incomplete. For better comparison with trap material, laboratory-made aggregates ("marine snow") from estuarine water were incubated with and without $HgCl_2$. After 8 days, rRNA in the mercury treatments was mostly degraded, particularly at room temperature. Exoenzyme activity was reduced, but not eliminated. Potential implications of this work are twofold. First, the effectiveness of mercuric chloride as a poison and a preservative may depend on sample type and temperature. Second, rRNA may persist in dead cells under some conditions, so it may not always reflect the currently active population.

Controls on Methane Oxidation at Seeps Sites in the Gulf of Mexico

J. J. Battles, M. A. Saxton, S. B. Joye
University of Georgia, Athens, GA

The Deepwater Horizon oil spill resulted in the release of massive amounts of methane gas into the waters of the Gulf of Mexico. This release resulted in a significant stimulation in the activity and abundance of methanotrophic bacteria as described by Crespo-Medina *et al*. 2014. As the methane plume dissipated and other nutrients were drawn down the methanotrophic bacterial community saw significant changes in abundance and composition. Aerobic methane oxidation is a microbially-driven process that leads to net removal of methane from the environment. These methanotrophic bacteria act as a biological filter, utilizing methane that may otherwise be released from the ocean to the atmosphere. To better understand the factors regulating methane oxidation in the pelagic ocean environment, we will be performing a series of experiments exploring the factors limiting this metabolism, potentially nutrient concentrations such as N, or Fe, or predation, on methane oxidation rates and methanotrophic bacterial community structure. We incubated water collected from natural methane seeps in the Gulf of Mexico under a range of methane concentrations including nutrient and trace metal additions, as well as grazing inhibition. We hypothesize that changes in methane concentration drive changes in methanotroph activity and diversity, leading to different methane oxidation regimes. We will identify limiting factors and interactions that control methanotrophic bacterial community structure and activity, providing insights into how the natural methanotrophic bacterial community will respond to future large-scale methane releases.

Effects of Temperatures and Oil Concentrations on Biodegradation of Light Louisiana Sweet Crude Oil in Gulf Coastal Seawaters

J. Liu, A. Kang, K. Lanpher, Z. Liu
The University of Texas at Austin Marine Science Institute, Port Aransas, TX

Understanding the biodegradation rates and fate of crude oil is critical to evaluate the impacts of oil spill in marine environments. In this study biodegradation of different crude oil concentrations (50, 100, 200, 400, and 800ppm) was investigated in seawaters at 4°C and 24°C in the dark for 50 days. n-Alkanes (C9-C37) were analyzed. They decreased exponentially during the initial time incubations (day 0 to 12), and then gradually plateaued after day 28 at 24°C. The degradation rates differed significantly between 4°C and 24°C and among different oil concentration incubations. At 24°C, alkanes were rapidly degraded from 6.0 to 3.4 μg/mL within 5 days in the 50ppm oil incubation, compared to a decrease from 79.7 to 64.3 μg/mL with 800ppm oil addition. In the 400ppm experiments, the final biodegradation rate was 41% at 24°C, compared to 25% at 4°C. Total bacterial abundances increased with additions of crude oil, but in different patterns. At 24°C, bacteria decreased first, and then gradually increased thereafter. In contrast, there was no lag phase at 4°C. The relative high bacterial abundances were observed in 50 and 100pm experiments at 4°C, which was contrary to the high oil concentration experiments at 24°C. The results suggested some saturated alkanes are recalcitrant and resistant to biodegradation in the dark, or that their degradation was limited by nutrients. Nutrient concentrations, aromatic hydrocarbons, and bacterial community structure will also be presented.

Biodegradation of Oil by Microorganisms from Marine Sediments at High Pressure

A. Valladares[1], E. M. Su[1], J. Martín Juárez[1], M. Schedler[1], G. Gust[1], M. Finck[2], P. Jaeger[2], R. Mueller[1]
[1]Hamburg University of Technology, Hamburg, Germany, [2]Eurotechnica GmbH, Bargteheide, Germany

In 2010, the Deepwater Horizon (DWH) oil rig explosion in the Gulf of Mexico caused the deepest oil spill in history (1.5 km~150 bar pressure. The biodegradation of oil in high-pressure environments, like the seabed and its boundary layer close to the DWH, is insufficiently understood. The oil-biodegradation capability of bacteria contained in sediments collected from differently spill-impacted seabed sites around the DWH in the Gulf of Mexico was compared at 1 bar vs. 150 bar. The oil biodegradation experiments were made in a high-pressure reactor of the following characteristics: 25 mL volume, 200 bar maximum operation pressure, online pressurized sampling and adjustable temperature. The biodegradation of oil was determined indirectly by measuring the oxygen concentration with optochemical sensors. Preliminary results indicate that the best conditions for biodegrading oil using seabed sediments as inocula were at 5°C, 150 bar pressure when using mineral media supplemented with 3% NaCl. Different microbial populations developed when the sediments were incubated at 1 bar compared to 150 bar. The final objective of the project is to understand and quantify the benthic biodegradation of oil at high pressures by natural microbial communities at in-situ conditions under oxic and anoxic environmental conditions and to establish both activity rates for modelling hydrocarbon biodegradation and appropriate proxies for high pressure environments.

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

On the Challenge of Remote Estimation of Surface Oil Volume in the Ocean: Examples from Satellite and Airborne Measurements

S. Sun, C. Hu
University of South Florida, St Petersburg, FL

Optical remote sensing is one of the most commonly used techniques in detecting oil in the surface ocean. This is because that oil has different optical properties from the background water and oil can also modulate surface waves, providing a contrast to facilitate delineating oil-water boundary. Estimating oil volume or thickness from the delineated oil footprint is much more difficult and currently represents a major challenge in remote sensing of oil spills. Several studies have attempted to associate reflectance spectra with oil thickness from laboratory experiments under well controlled conditions, where such established relationships were used to quantify oil thickness from remote sensing measurements from either spaceborne or airborne sensors. Here, through assembling some of the published lab-based spectra and analyzing remotely sensed spectra from several satellite and airborne sensors (MERIS, MODIS, AVIRIS, and MISR) during the Deepwater Horizon oil spill, we evaluated the potentials and challenges in remote sensing of oil thickness in the marine environment. Comparison between the lab-based results showed diversified spectra magnitudes and shapes possibly due to their difference in oil type, oil-water mixing rate, and measurement conditions. Furthermore, reflectance spectra extracted from oiled pixels of remote sensing imagery showed difference from all lab-based results. Thus, estimating surface oil thickness still represents a major challenge for the remote sensing community. This research aims to demonstrate the challenge while discussing possible solutions in future research, for example through step-wise schemes to combine classification and type-specific algorithms.

A Nearshore Dynamics Model of Oil Spills

J. M. Restrepo[1], C. Michosky[2], S. Venkataramani[3], C. Dawson[2]
[1]Oregon State University, Corvallis, OR, [2]University of Texas, Austin, TX, [3]University of Arizona, Tucson, AZ

The shallow end of the continental shelf is the home of hundreds of oil rigs. We exploit the dynamic regime, together with filtering, to devise a mass-preserving coupled ocean/wind/oil model, capable of capturing the depth-averaged dynamics of sea surface and sub-surface oil. A preliminary overview of the model and its capabilities will be presented.

Observed Downwelling in a Warm Core Eddy during Hurricane Isaac's Intensification

B. Jaimes, **L. K. Shay**
RSMAS/University of Miami, Miami, FL

Measurements of the three-dimensional oceanic response to hurricanes in the Gulf of Mexico are critical to accurately evaluate dynamical loading on marine oil facilities, as well as mixing and dispersion of oil products through the water column. As part of the NOAA Intensity Forecasting Experiment and in support of Deep-C, airborne expendable bathythermographs, conductivity-temperature-depth, and current profilers were deployed from NOAA WP-3D aircraft in tropical cyclone Isaac during four research flights to measure upwelling and vertical mixing over the upper ocean close to the Deepwater Horizon site. Based on radar altimetry, these probes were deployed in Gulf of Mexico's eddy features during the intensification of Isaac into a hurricane. These measurements suggest isotherms' downwelling up to 60 m over a 12-h interval, or twice the upwelling strength underneath the storm's center. This displacement occurred over a warm core eddy located on Isaac's left side, where the ensuing upper-ocean warming was ~8 kW m-2 where sea surface temperatures exceeded 28C during Isaac's intensification. Rather than with just Ekman pumping, these observed upwelling-downwelling responses were consistent with a vertical velocity, derived from the geostrophic vorticity balance that considers geostrophic flow strength (eddy Rossby number), Coriolis parameter, aspect ratio, oceanic mixed layer depth, storm's radius of maximum winds, and surface stresses. These empirical results underscore the need for initializing coupled numerical models with realistic ocean states to correctly resolve the three-dimensional upwelling-downwelling responses to hurricanes that will affect the dispersion of oil products in extreme wind conditions.

Effects of Swell on Transport and Dispersion of Oil Plumes within the Ocean Mixed Layer

B. Chen[1], D. Yang[2], **M. Chamecki[1]**, C. Meneveau[2]
[1]Pennsylvania State University, University Park, PA, [2]Johns Hopkins University, Baltimore, MD

When the oil from deep water blowouts reaches the ocean mixed layer (OML), the transport and dilution of the plume is strongly affected by the interplay of the wind and wave fields and resulting Langmuir turbulence. Typically, the wind-driven wave is nearly aligned with wind direction. However, the swell wave, which is left over from previous and remote wind-generation events, can have an arbitrary orientation relative to the local wind. In this study, we used large eddy simulation (LES) to capture the influences of the misalignment between wind and wave on oil. Results show that even the main direction of transport, characterized by the center line of the time-averaged surface plume, depends on the alignment between wind and waves and droplet size. Plumes of large droplets tend to follow the mean surface current direction, while the surface plume of small droplet does not. The inclination angle of small droplet surface plumes changes little as misalignment between wind and wave increases. This is because small droplets have less buoyancy and respond to the flow direction within the entire OML (including effects of Ekman transport). The eddy viscosity and diffusivity are also calculated based on LES data. Their magnitude decreases by more than 50% as the misalignment changes from 0 to 90 degrees. A framework to include these effects in K-profiles parameterizations (KPP) is also discussed. This study is supported by a Gulf of Mexico Research Initiative RFP-II research grant.

Diel Vertical Migrations of Zooplankton and Turbulent Mixing Numerical Simulation in Relation to Potential Oil Spills

C. W. Dean[1], A. V. Soloviev[1], T. M. Frank[1], A. C. Hirons[1], J. Wood[2]
[1]Nova Southeastern University, Hollywood, FL, [2]Ocean Data Technologies, Marstons Mills, MA

Zooplankton that undergo diel vertical migrations (DVM) can have an impact on oil transport through the water column and oil can have a negative effect on the health of the organisms. Recent studies (Dewar et al. 2006; Wilhelmus and Dabiri 2014) suggest that DVM of zooplankton may have an impact on ocean mixing, though details are not completely clear. In our work, we observed a strong sound scattering layer undergoing DVM via a bottom mounted ADCP at 244 m isobath in the Straits of Florida. A computational fluid dynamics model was used to reproduce the effects of DVM on the velocity field and turbulence signature. The model was initialized with idealized (but based on observation) density and velocity profiles in the Gulf Stream. Particles, with buoyancy adjusted to serve as a proxy for vertically swimming zooplankton, were injected to simulate DVM cycles. Model results showed a significant increase in the dissipation rate of turbulent kinetic energy at concentrations above 100 kg m-3 (though direct relation of the turbulence produced by buoyant particles and swimming organisms isn't straightforward). Slight distortion of the current velocity profile was also produced by the model, which was consistent with an 11 month ADCP observational data set in the Straits of Florida. Turbulence measurements were not available in the Straits of Florida experiment. However, we find our model results qualitatively consistent with turbulence measurements by Kunze et al. (2006).

A Study of Land/Sea Breeze and Critical Latitude Resonant Effect Using a High-Resolution Ocean-Atmosphere Coupled Model of the Gulf of Mexico

C. Hsu, P. Chang, J. Kurian, R. Montuoro
Texas A&M University, College Station, TX

Near-initial waves (NIWs) are prominent features of the Gulf of Mexico and can potentially elevate mixing levels in the water column, thereby affecting oil spill dispersion. In the Gulf of Mexico, land/sea breeze provides an important source of energy for NIWs, but its effect has not been fully quantified. In this study, we examine land/sea breeze circulation using a fully coupled high-resolution ocean-atmosphere model and various observations in the Gulf of Mexico. The model explicitly resolves diurnal cycle and is capable of directly simulating the effect of land/sea breeze circulation on NIWs in the Gulf of Mexico. We will assess the impact of land/sea breeze circulation on NIWs by comparing the NIW activity in the fully coupled model simulation to that simulated by an ocean-only model forced by atmospheric fluxes that contain no land/sea breeze circulation. We will discuss the potential impact of land/sea breeze on NIW-induced ocean mixing in the Gulf of Mexico.

Preconditioning with Level-Set Method for Air-Water Two-Phase Flow Simulations

D. Espinal, G. Zha
University of Miami, Coral Gables, FL

2D and 3D incompressible flows are solved using preconditioned RANS equations coupled with the Level-Set equation. High order WENO schemes are used with a E-CUSP Riemann solver. For viscous effects a Large-Eddy Simulation (LES) turbulence model is used. The Level-Set equation has a

conservative form and is used to determine equations-of-state and interface jump conditions. Validation is first performed for low speed, low Reynolds number laminar boundary layer flows for water and air comparing flat-plate simulation results with the theoretical solution from Blasius. Next, 2D and 3D Rayleigh-Taylor instabilities are simulated to show preconditioning capability to solve a two fluids problem. More cases with air-water two-phase flow simulations is in progress and will be reported in the final report.

The Air-Sea Interface in the Presence of Oil and Dispersants: Multi-Phase Modeling Coordinated with Laboratory Experiments

A. V. Soloviev[1], M. McGauley[1], B. Hamilton[1], B. Haus[2], N. Laxaque[2], D. Ortiz-Suslow[2]
[1]Nova Southeastern University, Dania Beach, FL, [2]University of Miami Rosenstiel School of Marine and Atmospheric Science, Miami, FL

A multi-phase computational fluid dynamics model with 0.2 mm vertical resolution has been implemented in ANSYS/Fluent for simulating small-scale processes at the air-oil-water interface. Effect of dispersants has been included via modification of the water-oil surface tension coefficient. The numerical simulation was conducted in parallel with laboratory experiments at the University of Miami Air-Sea Interaction Salt Water Tank (ASIST). Coordinated numerical and laboratory experiments appeared to be very useful for the model verification. We have modeled a range of wind speeds, up to hurricane force winds, and cases of the air-water interface with surface active materials (as a proxy for dispersants), thin oil layer and thick oil layer. Under low and moderate wind speed conditions, surface tension effects dominated oil spill dynamics. Under very high wind speed conditions, we observed disruption of the air-water interface in the form of “fingers” or thin sheets of water fragmenting into spume. The velocity difference across the aqueous viscous sublayer in the presence of gravity-capillary waves has been reproduced with this model and is consistent with previous laboratory experiments. The aim of this activity is to develop an advanced parameterization of hydrocarbon fluxes, based on the air-sea interface microphysics and compatible with the larger scale ocean and atmosphere models.

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

Natural Granular Materials as a New and Effective Crude Oil Treatment Method

D. Boglaienko, B. Tansel
Florida International University, Miami, FL

Various methods exist to treat crude oil spills. A new sand-oil treatment method was investigated. The method is based on the oil density changes after granular materials are applied on top of the floating oil that makes it to sink as large aggregates without breaking. We conducted three series of experiments. First series was aimed to find particle sizes that aggregate with oil. Second one analyzed amount of granular material needed. The purpose of third series was to study impact of granular material moisture content on the aggregation. Our experiments were designed, using South Louisiana crude oil and limestone/quartz sand with different particle sizes. Coarse (4.75-2.00 mm), medium (2.00-0.30 mm), and fine (< 0.30 mm) limestone; quartz, as fine sand (< 0.30 mm). Granular material was applied in

amounts of 0.5, 1.0, 1.5, 2.0, and 3.5 g on top of 1 mL of floating oil. Moisture content of the natural material was 0, 25, 50, and 100%. All experiments were conducted in 125 mL Erlenmeyer flasks with 100 mL of synthetic sea water (34% of salinity); at the room temperature. Flasks were placed on a shaking table (150 rpm) to simulate turbulence on the water surface. Our results showed that granular materials of fine and medium particle sizes create oil-sand aggregates that sink rapidly and stay at the bottom in a steady form for a long time (over months). The amount of particles needed to capture >70% of oil is 2.0 g. Sufficient amount of oil can be captured only by 100% dry granular material. The method can be also utilized to capture the floating oils in concentrated forms mixed with sand with simple subsurface capture mechanisms.

The Hydrodynamics of a Subsurface Oil Release in a Flume Tank

B. J. Robinson[1], T. L. King[1], R. N. Conmy[2], S. A. Ryan[1], M. C. Boufadel[3], H. Niu[4]
[1]Fisheries and Oceans Canada, Bedford Institute of Oceanography, Dartmouth, NS, Canada, [2]U.S. Environmental Protection Agency, Office of Research and Development, NRMRL, Cincinnati, OH, [3]Department of Civil and Environmental Engineering, New Jersey Institute of Technology, Newark, NJ, [4]Department of Engineering, Dalhousie University, Halifax, NS, Canada

The fate and transport of oil following an accidental underwater release is strongly dependent on the resulting oil droplet size distribution (DSD). During the Deep-Water Horizon incident in 2010, plumes of dispersed oil were detected in the subsurface water column up to 35 km away from the damaged wellhead. To evaluate the horizontal transport of oil droplets following a subsurface release, a new meso-scale flume tank was constructed. The tank has dimensions of 30 m x 2 m x 0.6 m (LxWxH) with an operational water volume of 30,000 L, and it is equipped with a high-flow system that can generate water currents of up to 5 cm s-1. An injection system allows oil heated to near reservoir temperature to be released at depth at various pressures through an orifice (2.4 mm i.d.). Under simulated marine environmental conditions, 48 experiments were conducted to evaluate how factors such as dispersant-to-oil ratio (DOR: 0, 1:20, 1:100, and 1:200), oil type (Alaskan North Slope and IFO 120), and high current velocity affect the transport of a subsurface oil release. These factors were evaluated by monitoring the DSD using particle size analyzers (LISST), in-situ fluorometers to track and monitor the subsurface oil plume as well as through the collection and chemical analysis of discrete water/effluent samples. In addition, the effect on the release of surface volatile emissions when dispersant is used to treat a subsurface oil release was studied. Results of this experimental program will be presented, along with discussion about how the generated physical measurements will be integrated into new and existing deep-water blowout models.

Comparative Analysis of Floating Crude Oil Removal by Capturing It with Natural Material vs Dispersion of Oil with Corexit 9500A in Presence and Absence of Granular Particles

D. Boglaienko, B. Tansel
Florida International University, Miami, FL

Mobility of crude oil is reduced when dry granular material is applied on top of an oil slick. In this case natural granular material (limestone, quartz sand) creates oil aggregates, which settle to the bottom (experiments were conducted in 125 mL volumetric flasks) capturing up to 90% of crude oil. Presented study was aimed to compare removal of floating crude oil by capturing it with dry granular material and

removal (i.e. dispersion) of floating oil by Corexit 9500A dispersant in presence and absence of granular particles. We conducted our experiments with such parameters: 100 mL of 34% salt water, 0.5 mL of South Louisiana crude oil, 1:25 dispersant to oil ratio, 2 g of limestone with particle size 2.00-0.30 mm, 200 rpm, and room temperature. Our results showed that floating crude oil capture and removal by natural granular material was almost 1.5 times more effective than its removal by dispersion with Corexit 9500A (42 vs 27%). However, presence of granular particles in salt water did not increase dispersant effectiveness (20-25%).

A Quantitative Insight into the Growth of *Alcanivorax borkumensis* under Different Inoculation Conditions

M. Bookstaver[1], M. Godfrin[1], A. Bose[2], A. Tripathi[1]
[1]Brown University, Providence, RI, [2]University of Rhode Island, Kingston, RI

Alcanivorax borkumensis is a hydrocarbon degrading bacterium found to dominate bacterial communities in marine regions containing high levels of hydrocarbons. It has been linked to oil degradation around oil spill sites, thus it has potential to be used actively in oil spill remediation. Here we investigate the effect of solution and interfacial conditions on the growth of *Alcanivorax borkumensis*. We show that providing *Alcanivorax borkumensis* with dissolved organic carbon as an energy source in solution leads to shorter lag times prior to hydrocarbon utilization at the oil-water interface. Hence, *Alcanivorax borkumensis* can be encouraged to utilize n-alkanes present at the surface of the system quicker by supplementing the system with dissolved organic carbon in the form of a fertilizer. For fixed oil-water interfacial areas, the growth rates of bacteria show weak dependence on the initial bacteria concentrations, however, increasing bulk interfacial area leads to higher bacterial growth rates due to an increased amount of available surface area for degradation. Therefore, allowing the oil to spread over a larger surface area may increase the rate of degradation by *Alcanivorax borkumensis*. We also explain our experimental finding using a model for bacteria growth. To our knowledge, this is the first study to offer quantitative insight into how *Alcanivorax borkumensis* can be actively supported in their utilization and degradation of oil for the bioremediation of marine oil spills. Future studies will involve using this same technique to quantify the growth of other types of bacteria under certain conditions. Furthermore, the same technique can be modified for larger scale experiments.

Bacterial Adhesion and Biofilm Formation over Surface with Printed Oil Micro-Droplet Array

M. Jalali-Mousavi[1], K. J. Stebe[2], J. Sheng[1]
[1]Texas Tech University, Lubbock, TX, [2]University of Pennsylvania, Philadelphia, PA

Oil spill pollution resulting from accidents has affected several regions around the globe. Biodegradation has been proposed as an effective and environmental friendly way of removing the crude oil form the polluted seawater. Despite the vast interest in bioremediation, key mechanisms and processes of oil-bacteria interactions have not been well understood. In prior studies, we have fabricated solid substrates with micro-scale chemical textures using soft lithography and novel surface functionalization. The surfaces have been applied to study the bacteria-surface interactions and the key processes of biofilm formation over the chemical surface textures. A strong correlation between biofilm morphology and substrate textures was found. In current work, we have furthered our investigation on biofilm

formation over oily micro-textures. To facilitate the study, we have successfully created micro-droplet arrays of crude oil with various sizes and arrangement over a glass substrate. The oil droplet texture was formed by micro contact printing of crude oil using PDMS stamps. The fabricated micro-droplet textures have dimensions ranging from 5µm to 50µm with various shapes. The oil patterned surface has been incorporated into a microfluidic device, which allows us long term observation of dynamic processes. The dynamic interactions such as swimming, dispersion, attachment, detachment, and adsorption between bacteria and micro droplet patched oily surface under flow conditions are investigated in-situ. The growth rates and morphology of bacterial colony and biofilm are also studied and reported.

Collision Rates between Oil Droplets and Particulate Matter: Mechanisms and Effect of Droplet Size Distribution

E. Variano, R. Lambert
University of California, Berkeley, Berkeley, CA

Rising oil droplets can scavenge particulate matter that is suspended or descending in the water column. This process can lead to oil-mineral aggregates which may become negatively buoyant. To understand the possible effects of chemical dispersant, we explore the effect of droplet size on the collision rates. We calculate the relative rate at which oil is removed from the water column, as a function of droplet size at constant oil concentration. The results of the comparison show that for a constant volume of oil, droplet size does alter the amount of oil that collides with particulate matter. The findings suggest that using chemical dispersant on deep-sea oil spills to reduce droplet size will alter the total volume of oil that attaches to particulate matter. The result is non-monotonic: the initial and final droplet size determines whether droplet size reduction increases or decreases the volume of oil that attaches to particulate matter. When droplets are reduced in size to a final size greater than roughly 10 microns, this reduction in droplet size reduces the volume of oil that attaches to particulate matter. The results of this study are based on an analytical evaluation of three dominant collision mechanisms responsible for bringing marine floc and oil droplets into contact: Brownian diffusion, differential sedimentation, and turbulent diffusion. We model the collision process using existing collision kernels derived using the particle pair probability method.

Novel Insight into the Role of Heterotrophic Dinoflagellates in the Fate of Crude Oil in the Sea

R. Almeda[1,2], T. Connelly[1], C. Hyatt[1], **E. J. Buskey[1]**
[1]University of Texas at Austin, Port Aransas, TX, [2]Technical University of Denmark, Copenhagen, Denmark

We present the first evidence of ingestion and defecation of physically or chemically dispersed crude oil droplets (1-86 µm in diameter) by heterotrophic dinoflagellates, major components of marine planktonic food webs. At a crude oil concentration commonly found after an oil spill (1 µL L-1), *Noctiluca scintillans* and *Gyrodinium spirale* grew and ingested ~0.37 µg-oil µg-C dino-1 d-1, which could represent ~17% to 100% of dispersed oil in surface waters during a dinoflagellate bloom. Egestion of faecal pellets containing crude oil by dinoflagellates could contribute to the vertical flux of toxic petroleum hydrocarbons in the sea. Our study indicates that crude oil ingestion by heterotrophic dinoflagellates is a noteworthy route by which petroleum enters marine food webs and a previously overlooked biological process influencing the fate of crude oil in the sea after spills.

Simulation of Droplet Formation Process and Transport Due to Wave Actions during the Deepwater Horizon Oil Spill

L. Zhao[1], M. Boufadel[1], K. Lee[2], T. King[3], B. Robinson[3]
[1]New Jersey Institute of Technology, Newark, NJ, [2]Commonwealth Scientific and Industry Research Organization (CSIRO), Perth, Australia, [3]Bedford Institute of Oceanography, Department of Fisheries and Oceans, Dartmouth, NS, Canada

Under the action of waves, the coherent oil film floating on the water surface is dispersed into small droplets and get advected and spread in the water column. In this paper, the numerical droplet size distribution model, VDROP was coupled with a CFD wave model to predict the dispersion of oil due to waves in the marine environment. The model was validated against literature data in association with the wave tank experiments. Then, based on the local ocean environment of DWH blowout, the possible range of oil droplet sizes in the subsurface water column in the DWH site were obtained, and the transport pathways were predicted. Scenarios by varying the interfacial tension to simulate the addition of dispersants were also conducted.

Chemical Dispersants: An Oil Biodegradation Friend or Foe?

S. Rahsepar, M. Smit, **A. Langenhoff**
Wageningen University, Wageningen, Netherlands

The effect of chemical dispersants on the oil biodegradation is still a matter of dispute, as both inhibition and enhancement of oil biodegradation is described in the literature. In this presentation, we will show the pros and cons of the dispersants application. We will discuss the effect of various dispersants to oil ratios, the importance of the present microbial community, and turbulent or static condition on the biodegradation rate of either crude or weathered oil. We used an n-alkane degrading culture *Rhodococcus qingshengii TUHH-12* to study the degradation of crude or weathered oil in batch experiments at three dispersants to oil ratios (0:1, 1:100 and 1:20). Similar experiments were performed with *Pseudomonas putida F1*, an aromatic degrading culture. Both cultures were also used together to study their combined effort on the degradation of oil in presence of dispersants. Our results indicate that a low dispersants concentration does not enhance the oil biodegradation and even decrease the oil biodegradation at higher concentrations. However, this effect is less when both cultures are present, and most components of the oil are degraded. With this research, we have learned about the effect of dispersants on the biodegradation of oil, and especially the effect that is exposed by the individual components of oil, such as alkanes and aromatic hydrocarbons. The outcomes of this study will be used to improve the decision support system to select the most effective response option at oil spills.

Quantification of Copepod Escape Success after Varied Exposure to Crude Oil and Chemical Dispersants

M. Mei, B. J. Gemmell, E. J. Buskey
University of Texas at Austin, Port Aransas, TX

Copepods account for approximately 75% of marine zooplankton and form key links in food webs. Since these organisms rely on powerful escape swimming behavior to avoid predators, understanding how sublethal concentrations of oil and/or dispersants affect this behavior is an important consideration.

Using a siphon flow of ~2.0 mL s^{-1} to mimic suction of predatory fish, we quantified copepod escape behavior using high resolution, infrared videography. *Acartia tonsa* were incubated for 24 hours with crude oil and/or dispersant (Corexit 9500A) at oil concentrations of 5, 2.5, and 1.0 µL L^{-1} (1:20 dispersant to oil). Exposures of 5 µL L^{-1} crude oil were also made for 24, 18, 12, and 6 hrs. Results show that after 24 hours, dispersant and dispersant-treated oil had significantly higher copepod capture rates at concentrations of 5 and 2.5 µL L^{-1}, with dispersant-treated oil having the greatest effect. Dispersant alone resulted in high capture rates at all concentrations tested suggesting that even low concentrations of dispersant may be enough to interfere with copepod escapes. At varied exposure times, capture rates peaked at 12 hours for dispersant only and oil only treatments. For dispersant-treated oil, susceptibility increased linearly with time. No differences were observed in the kinematics of escape behaviors among treatments. These results suggest exposure to dispersant or dispersant-treated oil inhibits either detection of fluid displacement or the initiation of an escape response.

Radium Isotopes as Conservative Tracers of Hydrocarbon Transport Through the Water Column

R. Peterson[1], L. E. Peterson[1], J. P. Montoya[2], S. C. Weber[2], C. D. Meile[3], S. B. Joye[3]
[1]Coastal Carolina University, Conway, SC, [2]Georgia Institute of Technology, Atlanta, GA, [3]University of Georgia, Athens, GA

Following the Deepwater Horizon blowout, neutrally-buoyant hydrocarbon plumes were observed spreading laterally from the well. This observation led to the realization that we do not have a suitable proxy to trace the time scales of such transport pathways, which is vital to understand the time frames over which in-situ microbial degradation processes can occur. We are investigating the potential to use naturally-occurring radium isotopes (known to be enriched in hydrocarbon reservoirs) as such a tracer through the water column. The wide range of radium isotope half-lives (3.6 days to 1600 years) offers both radioactive and 'stable' analogs over the time scales of transport. We present new data from several natural hydrocarbon seeps as well as from the Hercules 265 rig blowout in 2013 to demonstrate the utility of radium as a useful proxy to determine the time scales of hydrocarbon transport. When synoptically sampled throughout a laterally-spreading hydrocarbon plume, such as that which occurred in bottom waters around the Hercules 265 rig blowout, radium isotope activity ratios provide a time since discharge of various samples out to about 3 weeks. This method offers the most promise when coupled with a technique to identify the location of a neutrally-buoyant plume, and when integrated with in-situ microbial oxidation rates.

Chromatographic Separation and Characterization of Source and Surface Oil from the Deepwater Horizon

T. A. Grusenmeyer, A. Lawrenson, A. M. Kulik, N. A. Leed, R. H. Schmehl
Tulane University, New Orleans, LA

In an attempt to examine the fate of resins and asphaltenes following weathering at the gulf-air interface, samples of source and surface oil were systematically separated and characterized. The asphaltenes and resins were initially separated from the bulk and further resolved using a combination of 2-D preparative thin layer chromatography (TLC) and column chromatography. The resulting fractionated samples were then characterized using MALDI-TOF mass spectrometry, UV-Vis absorbance

spectroscopy, and UV-vis and NIR luminescence spectroscopy. The observed changes in chromatographic behavior, spectroscopic properties, and mass spectrometry data will be presented.

Effect of Bacteria and Diatom Interactions on Mechanical Properties of Oil-Water Interfaces

L. Vaccari[1], L. Tran[1], T. H. R. Niepa[1], J. Sheng[2], D. Erdner[3], M. Goulian[1], K. J. Stebe[1]
[1]University of Pennsylvania, Philadelphia, PA, [2]Texas Tech University, Lubbock, TX, [3]University of Texas Marine Science Institute, Port Aransas, TX

We have shown that biofilms form at alkane-water interfaces with significant elastic moduli, acting to effectively encapsulate the oil. Here, we extend that work to study bacteria-diatom interactions. Diatoms and bacteria have existed in the same ecosystem for hundreds of millions of years. Because of this long coexistence, it is expected that the two kingdoms interact and influence the growth or decay of one another's colonies. We have seen the formation of strong, elastic films by purely bacterial biofilms on oil droplets. Diatoms incorporate into these films; we explore the effects of diatom inclusions on the biofilm's mechanical properties, and the role of oil droplets in capturing and impacting diatom populations. Experiments are performed on a model oil (hexadecane) and for crude oil interfaces.

Characterization of > 30,000 Newly Discovered Biotic and Abiotic Petroleum Transformation Products and Their Potential Impact on Stable Droplet Formation

R. P. Rodgers[1], S. Rowland[2], H. Chen[1], Y. Corilo[1], A. McKenna[1], A. Clingenpeel[2], J. Jarvis[1], J. Putman[1], A. Marshall[1,2]
[1]NHMFL Florida State University, Tallahassee, FL, [2]Florida State University, Tallahassee, FL

The chemical transformation of petrogenic carbon in the environment yields an incredibly complex mixture of products that can dramatically alter their chemical functionalities. The changes affect toxicity, solubility, emulsion/mousse formation, aggregation, and ultimately, bioavailability. Molecular level, qualitative understanding of the (predominately) oxidative weathering is hampered by the immense complexity of the unaltered oil and multiplicative increase in complexity post-oxidation. A large fraction of the unaltered oil that was initially accessible by GC-methods is chemically transformed into species that preclude GC based analyses. Thus, the petrogenic transformation products and their potential to form undesirable future contaminants remain unknown. However, recent advances in analytical methodology and instrumentation now allow an unprecedented, molecular-level insight into these complex systems. The detailed compositional analysis of oil-impacted areas along the Gulf of Mexico coast over the past 4 years, revealed tens-of-thousands of previously unidentified biotic and abiotic transformation products that have persisted. Here, we highlight our efforts to characterize these oxidized transformation products, identify their oxygen functionalities, and demonstrate how they affect physical/chemical behavior (stable emulsion / droplet formation). 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.

Effects of Oil and Dispersants on Swimming Behaviors of Copepods Exposed to High Hydrostatic Pressure

A. Nihongi[1], T. Consi[1], P. Hinow[1], T. Nagai[2], M. Uttieri[3], E. Fennimore[4], A. Genin[5], J. R. Strickler[1]
[1]University of Wisconsin-Milwaukee, Milwaukee, WI, [2]Tokyo University of Marine Science and Technology, Tokyo, Japan, [3]University of Naples, Naples, Italy, [4]eAchieve Academy, Waukesha, WI, [5]The Hebrew University of Jerusalem, Jerusalem, Israel

Our current work suggests common planktonic invertebrate species are capable of altering the fate of oil. For example, copepods ingest oil droplets, which are eliminated as fecal pellets. Little attention has been paid to the effect of oil droplets and dispersants on behaviors of zooplankton while the animals live at deep water. However, it is difficult to investigate changes in behaviors of zooplankton in situ in the deep of the water column. We have developed a deep-water simulator, a pressure chamber. This allows us to observe physiological changes, feeding behaviors, and swimming behaviors of zooplankton under an ambient pressure range equivalent to 0 to 3000 m depths. We observed the effect of oil droplets and dispersants in swimming behaviors of copepods at different ambient pressure. Over the range of pressure at 0m depth and 3000m depth, the buoyancy of the animals also changes as well as the characteristics of their feeding currents. The results will be demonstrated through videos.

Stochastic, Low Dimensional Parameterizations for the Aging of oil

S. Venkataramani[1], J. Restrepo[2]
[1]University of Arizona, Tucson, AZ, [2]Oregon State University, Corvallis, OR

"Oil" in the environment is a composite of hundreds or thousands of individual species, each with its own, and often widely different, physical and chemical properties. It is therefore a challenge to build models for oil fate that account for all of this complexity. We develop a framework using ideas from dynamical systems theory to build stochastic, low dimensional models for the aging/degradation of oil treated as an aggregate. The method has two key features (i) It gives a hierarchy of models with increasing complexity and the user gets to decide on the tradeoff between complexity and the fidelity of the model; (ii) The framework is Bayesian and it naturally allows for the incorporation of information from multiple, disparate data sources including lab experiments, field measurements, modeling and simulations. The resulting model is a (small) set of SDEs or Stochastic time-delay equations, that can be coupled with Oil dynamics/Ocean circulation models for Uncertainty quantification of Oil fate predictions on intermediate and longer time scales, and for data assimilation to improve the predictive skill of the combined model.

Quantifying Degradation Products of Louisiana Sweet Crude Oil in the Gulf Waters

X. Hu[1], H. Bacosa[2], Z. Liu[2]
[1]Texas A&M University - Corpus Christi, Corpus Christi, TX, [2]University of Texas at Austin - Marine Science Institute, Port Aransas, TX

Quantifying degradation products of crude oil is important in evaluating the fate and toxicity of oil spills in marine environments. While most studies have focused on traditional hydrocarbon analysis to weathered oil, little is known about the degradation products, such as CO2 and oxygenated hydrocarbons. From the oceanographic point of view, how the final product of microbial respiration - carbon dioxide evolves during oil degradation is unknown, despite that water column data shortly after

the Deepwater Horizon oil spill showed deviation in the oxygen and CO2 relationship from typical aerobic algal carbon remineralization. In this work we will present results from closed-system incubations of oil only and oil with Corexit dispersant under light and dark conditions, and examine how dissolved oxygen and CO2 (both concentration and stable carbon isotope) changes with time. Changes of petroleum hydrocarbons with time, including alkanes and aromatics, will also be presented.

Dynamics of Oil Droplet Impinging on Air-Water and Oil-Water Interfaces

S. Kim, J. Sheng
Texas Tech University, Lubbock, TX

We experimentally investigate the hydrodynamics of the crude oil droplet impinged upon a flat air-water and oil-water interface using a high-speed digital holography. The oil droplet driven to the interface by the buoyancy force exhibits complex kinematic sequences: (i) the interface deforms due to the approaching droplet; (ii) upon arriving, the droplet demonstrates bouncing and rolling kinematics; (iii) droplet reaches its quasi-equilibrium state and resides stably at the interface; (iv) rapid drainage of the thin film causes the fast expansion of the droplet and initiate the coalescence process; (v) rapid coalescence causes the ejection of secondary micro-droplet into bulk phase. These key interactions are shown to be affected by the interfacial energy landscape between oil droplet and the interface. To elucidate mechanisms, the interfacial energy landscapes are systematically varied by selecting proper interface pair, i.e. air-water, crude-water, and Hexadecane-water, as well as interfaces ladened with and without particles (Hawthorn fire clay, Bentonite western clay, Polystyrene particle and Diatom) to quantify kinematics. Preliminary results show that while interfacial tensions dominate the kinematics of the initial dynamic interactions (e.g. deformation, bouncing and rolling of droplets), hydrodynamic interactions of wake and interface are largely unaffected. Furthermore, particles ladened over clean interfaces can clearly stabilize the interface and prolong the coalescence, however, the patchiness of the oil contaminates over the interface substantially alter the coalescence time scales.

Interactions between Calanoid Copepods and Oil Droplets: They Take Big Ones and Make Smaller Ones

J. R. Strickler[1], M. Alcaraz[2], H. Jiang[3], J. Motschman[1], S. Horn[1], C. Keithrafferty[1], A. Nihongi[1]
[1]University of Wisconsin Milwaukee, Milwaukee, WI, [2]Institut de Ciències del Mar, Barcelona, Spain, [3]WHOI, Woods Hole, MA

Literature has it that calanoid copepods ingest oil droplets resulting at times in the statement that “copepods ate the oil slick.” We observed in great details interactions between suspended oil particles and free-swimming *Acartia grani* and *A. clausii*. We created the oil droplets with microfluidic devices. We observed the animals with high-speed digital holography. We enhanced the chances of observing interactions by constructing a Kreisel-type vessel. Main result was that a population of 16 micron diameter droplets was chopped up into a population of 4 micron diameter droplets in addition to the original population. Such a modification of the size-frequency distribution enhances the total surface area and changes the raising speed of the droplet population.

Estimating Rates of Hydrocarbon Biodegradation in Deep Waters of the Gulf of Mexico

A. E. Thessen, E. North
University of Maryland Center for Environmental Science, Cambridge, MD

Effectively managing petroleum in the environment, such as after an accidental spill, requires an understanding of how each of the individual chemicals interacts with environmental conditions. More information on the biodegradation rates of hydrocarbons in the deep waters of the Gulf of Mexico is needed to parameterize models of the fate and transport of subsurface oil spills. In an effort to deduce such biodegradation rates, we extracted hundreds of thousands of observations of hydrocarbons during and after the Deepwater Horizon oil spill from the GISR Deepwater Horizon database. Three different strategies for estimating biodegradation rates were applied: 1) calculating percent reduction in detection, 2) fitting a nonlinear model to account for both diffusion and degradation, and 3) normalizing compounds with the concentrations of slowly degrading compounds (pristane and nC35-nC40). Preliminary results indicate that there was enough data available for 68 compounds to calculate percent reduction in detection which ranged from 27.6% for n-C35 to 100% for benzene. The nonlinear fit method provided exponential decay rates for 13 compounds and the rates ranged from -0.0085 to -0.23 d-1 corresponding to 27 and 1 day half-lives, respectively. Normalizing concentrations of compounds to pristane was not successful: it was apparent that pristane was degrading in the subsurface. Analyses with the goal of normalizing with nC35-nC40 are ongoing and appear more promising. Decay rates estimated with these approaches will be compared with each other and discussed in relation to published laboratory and modeling results.

Evaluation of Droplet/Bubble Models for Subsurface Dispersant Application

E. E. Adams[1], S. A. Socolofsky[2], M. C. Boufadel[3]
[1]Massachusetts Institute of Technology, Cambridge, MA, [2]Texas A & M, College Station, TX, [3]New Jersey Institute of Technology, Newark, NJ

We have been conducting a two-part study to evaluate models pertaining to chemical dispersants applied sub-surface at a deep water blowout. The first part is an evaluation of models that predict droplet size distributions as a function of oil and gas properties, flow rates, release conditions, dispersant-oil-ratio, and other ambient variables. The droplet models generally fall into two classes: equations that predict characteristic droplet size as a function of dimensionless parameters such as the Weber and Reynolds numbers, and models that simulate the transient break-up and coalescence of droplets as they are transported with a plume. Models of both types are being compared against available laboratory and field data on droplet size distributions. In the second part of the study, differences in droplet sizes computed with different models, and with the same model with and without dispersants, are being analyzed through the lens of oil transport models. These include near-field plume models that simulate the effects of droplet size on oil transported in a plume, under the influence of ambient stratification and currents, and larger scale integrated oil transport models that simulate transport and fate over distances of 100s of km. A component of the second part was a recent workshop in which modeling groups were invited to use their particular integrated transport model to assess the efficacy of dispersants in a range of standardized case studies.

Intrusion Dynamics of Small Oil Droplets Released from a Deep Ocean Blowout

D. Wang, E. E. Adams
Massachusetts Institute of Technology, Cambridge, MA

Oil and gas jetted at high velocity, as occurred at the Deepwater Horizon incident, form a buoyant jet that tends to rise toward the surface. However, the smallest droplets separate (detrain) from the plume due to the effects of ambient stratification and current. Such small droplets are expected to be most prevalent when chemical dispersants are applied at the plume source. Our group has previously studied the critical droplet diameter below which detraining droplets enter an intrusion layer and how far they are transported within the intrusion, under linearly stratified but quiescent ambient conditions. Here we extend the study to flowing environments, by towing a source in a flume with dimensions 5m (L) x 1.2 m (W) x 0.6 m (H). Spherical glass beads with SG =2.5 are released as a dense slurry from a carriage at the top of the tank to simulate, in an inverted frame of reference, oil droplets rising from the sea floor. Dyed entrained fluid and particles in the plume and the intrusion layer are observed visually and the pattern of particle deposition (simulating the pattern of droplets rising out of an intrusion layer) is documented by weighing particles collected on a bottom sled towed with the source. The observed pattern of intrusion and deposition as a function of current speed, source buoyancy, stratification and particle/droplet slip velocity are being compared with an analytical model based on potential flow.

The Role of Span 80 as a Component of Corexit for Oil that Reaches the Shore

Y. Duan[1], C. G. Ezeh[1], R. Rausa[2], K. D. Papadopoulos[1]
[1]Tulane University, New Orleans, LA, [2]Eni, Rome, Italy

A transparent, miniature, cryolite-packed-bed capillary system is used to simulate microscopically the pressure-driven flow of crude oil-spill oil in random, natural porous media. Corexit 9500 and 9527 being dispersants of choice, the hypothesis was made that the Span-80 constituent of Corexit may enhance the attachment of oil on sands, sediments and other porous media it reaches after an oil spill occurs. We show that Span-80 alone clearly promotes the adherence (and persistence) of crude oil on cryolite. By allowing a three-phase system of crude oil, Corexit solution and cryolite to reach equilibrium, we explore the potential of mobilizing the oil by imposing a pressure gradient on the tube (capillary backed bed). An important result may be that the presence of Span 80 in Corexit may have the undesirable effect of enhancing the persistence of oil that reaches the shoreline.

Experimental Investigation on Effects of Dispersant on Breakup of an Oil Slick under Breaking Waves

C. Li, W. Ericksen, E. Rodbell, J. Katz
Johns Hopkins University, Baltimore, MD

This experimental study focuses on the generation and size and spatial distributions of airborne and subsurface oil droplets created by 24 cm high waves breaking on a controlled crude oil slick (MC252 surrogate) in a specialized wave tank. The effect of dispersant (Corexit 9500A) premixed with the oil at various dispersant to oil ratios (DOR) is also investigated. High speed visualization reveals processes affecting the entrainment of oil droplets and air bubbles, and the aerosolization of oil and water droplets. High speed digital holography is applied at multiple resolutions to yield distributions of the full range of droplet sizes (i.e. from ~1 μm to ~1 mm) above and below the water surface, and to track

droplet trajectories. Data obtained at multiple locations creates a spatiotemporal map of droplet and bubble sizes generated by the initial plunging and subsequent rollers. A single breaker entrains and aerosolizes oil droplets as it disperses a 500 µm thick, 65 cm2 oil slick over the full length of the 600 cm long wave tank. Introduction of dispersant reduces the size of subsurface oil droplets to micron and even submicron levels. Breaking waves for DOR as low as 1:100 generate extensive micro-sized oil threads that then break up into micron sized droplets. Micron to millimeter size airborne droplets are ejected and initially move in the same direction as the wave. Subsequently, after the wave crests, aerosolized droplets reverse their direction.

Interactions between Nanoparticles and Bacteria at Oil/Water Interfaces: A Dynamic Single Droplet Analysis System

M. Sihlabela[1], M. Godfrin[1], A. Bose[2], A. Chauhan[3], M. Levine[2], A. Tripathi[1]
[1]Brown University, Providence, RI, [2]University of Rhode Island, Kingston, RI, [3]University of Florida, Gainesville, FL

Alcanivorax borkumensis is a naturally occurring strain of marine bacteria that has been found to degrade alkanes. As such, the strain of bacteria presents an opportunity for a non-toxic, natural degradation of hydrocarbon molecules around oil spill sites in the marine environment. *Alcanivorax borkumensis* has been found to synthesize and release glucolipid biosurfactants that help the bacterium access and utilize the hydrocarbon phase by lowering the interfacial tension and forming oil droplets with increased interfacial area. An understanding of how these bacteria and their biosurfactant interact with oil droplets in a marine environment is essential in evaluating the effectiveness of the biodegradation processes. A variety of synthetic molecular surfactants and nanoparticles are able to stabilize oil droplets, and have been introduced for oil spill remediation. The introduction of surfactants has been found to aid the utilization of hydrocarbons by these oil-degrading bacteria. The effect of these nano-materials on the ability of marine bacteria and biosurfactant to interact with oil/water interfaces is important in understanding the fate of droplets in the post-spill environment. Single droplet analysis allows for the evaluation of interactions between bacteria, surfactants and the oil water interface, and a continuous flow system allows for the introduction of effects which mimic the marine environment. We have developed a continuous flow, single droplet platform to investigate the behavior of bacteria near oil/water interfaces. We have studied the effect of nanoparticles and synthetic surfactants on the activity of *Alcanovorax borkumensis* in seawater solutions at single hexadecane droplets.

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

Using Cyclodextrins for Pollutant Extraction and Array-Based Detection via Ternary Complex Formation in Complex Environments

N. Serio, M. Levine
University of Rhode Island, Kingston, RI

The rapid detection of various pollutants, including PAHs, PCBs, and pesticides, in a number of complex environments is crucial for both first responders and medical personnel. Gamma-cyclodextrin is a renewable cyclic oligosaccharide that is capable of simultaneously binding a fluorophore and aromatic

pollutant within its cavity. This three-component complex participates successfully in proximity-induced energy transfer, with excitation of the pollutant resulting in energy transfer to and emission from the fluorophore. The new emission wavelength is unique to each fluorophore-analyte combination, and is easily tunable via modification of the fluorophore component. Reported herein is the use of this unique system for the array-based detection of the aromatic toxicant analytes. This detection occurs in different environments, including oil spill oil, surface residual (tar) balls, phosphate buffered saline, and seawater, enabling efficient array-based detection in these systems. Cyclodextrins can also extract pollutants from these systems, which will aid in the detoxification of affected areas. The successful extraction and detection of these carcinogenic pollutants in complex environments highlights the utility this system in the various phases of oil spill response: the quantification, characterization, and detection of the analytes in complex environmental systems.

Effect of Solar Radiation on Transformation of Polycyclic Aromatic Hydrocarbons Trapped in Oil Spill Residues

G. John, F. Yin, Y. Han, J. S. Hayworth, T. Clement
Auburn University, Auburn, AL

Deepwater Horizon (DWH) oil spill residues in the form of Submerged Oil Mats (SOMs) and Surface Residual Balls (SRBs) continue to wash ashore on the gulf shores of Alabama to this day. Analysis of these oil spill residues showed that higher molecular weight polycyclic aromatic hydrocarbons (PAHs) continue to remain at the same concentration as that of the first arrived oil back in June 2010. This shows that, oil when travelling from the well head to the shore in the open ocean environment, degraded considerably. But when it reached the shore, it interacted with the nearshore sediments, transformed into SOMs and the degradation process reduced considerably. It is necessary to determine the fate of higher molecular weight PAHs that are trapped in these SRBs that are washing ashore. Photo-degradation is one of the significant degradation processes for the crude oil. In this research, we focus on the effect of solar radiation on the oil spill residue and study the transformation of PAHs trapped in it due to photo-degradation.

Novel NIR/SWIR Sensor System for the Early Detection and Monitoring of Offshore Oil Spills

G. M. Santos, M. Arnob, L. Liu, Z. Han, W. Shih
University of Houston, Houston, TX

We are developing an innovative sensor system for spatial detection of oil-on-water surfaces using multispectral near-infrared (NIR) and short-wavelength-infrared (SWIR) imaging and computational reconstruction. The study relies on the novel ultrasensitive detection mechanisms in the spectral information and thickness modulations of oil films recently modeled and experimented. With the use of a broadband light source, the oil-water interface is imaged to a Digital Micro-mirror Device (DMD). The full programmability of the DMD array for spatial sampling of the image leads to a smart acquisition scheme with less number of scene shots and shorter acquisition times as compared to its raster scan imaging counterparts. The spectral information of the reflected image is sent to a NIR/SWIR far-field spectrometer equipped with a 256-pixel line array InGaAs detector with high sensitivity over the 900-2500 nm spectral range. Since most hydrocarbons have unique extinction signatures within this range, the NIR/SWIR spectrometer is an efficient tracer of different oil components (i.e. iso-octane,

cycloalkanes). The spectral information (from the detector) and the spatial distribution (from the DMD) create a 3-dimentional data cube which can be processed to reconstruct the original image using compressive sampling technique. The proposed sensor system can potentially use solar light to detect and monitor the offshore oil spill. It would be a cost-effective sensing device that can be installed on multiple platforms to build a sensor network for oil spill trajectory surveillance.

Using Ramped Pyrolysis-Gas Chromatography-Mass Spectrometry to Evaluate Weathering Intensity of the Oil in Louisiana Salt Marshes following the Deepwater Horizon Oil Spill

M. M. Evans[1], B. E. Rosenheim[2], Z. Liu[1]
[1]Marine Science Institute, The University of Texas Austin, Port Aransas, TX, [2]College of Marine Science, University of South Florida, Tampa, FL

Determining the degree of oil weathering after an oceanic spill is important for evaluating the fate and toxicity of oil in marine environments. In this study we combined gas chromatography-mass spectrometry and ramped pyrolysis (Py-GC-MS) to analyze weathered oil collected from ocean surface and coastal marsh sediments following the Deepwater Horizon oil spill. Samples cover both spatial and temporal scales: surface slicks (2010), surface residual oil balls (SRBs) (2011-2012) and sediment samples (2010-2012) collected at Grand Isle and Bay Jimmy, Louisiana. Ramped pyrolysis radiocarbon analysis of a sample sub-set shows that organic carbon is derived largely from oil deposits. To identify the compounds present, we employed cryogenic trapping (cryo-trap) Py-GC-MS, which processes each sample as a number of thermal zones (temperature ranges within the pyrolyzer) and runs each separately through GC-MS. We found that lower-molecular-weight, volatile compounds are clearly detected in lower temperature zones (90-290°C), while more recalcitrant compounds are cracked and detected in higher temperature zones (290-530°C). This enables quantification of oxygenated hydrocarbons, which crack at high temperatures, releasing CO2. Preliminary results demonstrate CO2 increasing with weathering degree, suggesting increase in oxygenated hydrocarbons content. This is consistent with the notion that oxygenated hydrocarbons are a significant product of photooxidation and biodegradation; unfortunately, these toxic compounds have historically been ignored due to analytical limitations. Refinement of this method will remedy this problem, be cost, time and sample effective, and improve analysis of oil spilled in marine ecosystems.

Characterization of Submerged Oil Mat Samples from Coastal Louisiana

A. Lutz, V. Elango, **J. Pardue**
Louisiana State University, Baton Rouge, LA

Physical and chemical characterization of submerged oil mat (SOM) samples collected from Fourchon Beach, LA were performed on 17 unique samples collected in 2012 and 2013. The properties evaluated to characterize SOMs were; physical properties (dimensions, porosity, moisture content and density), composition of the SOM (identification of materials by manual separation), elemental composition by combustion, high-resolution transmission electron microscope and energy dispersive x-ray spectroscopy and alkylated PAH and alkanes by extraction and analysis using gas chromatography with a mass selective detector. Weathering indices were quantified by normalization of alkylated PAHs and alkanes with poorly biodegradable alkylated chrysenes and C30-hopane. Alkylated phenanthrenes, dibenzothiophenes, and chrysenes, were dominant PAHs in SOM samples. Alkanes C10-C15 were below

or close to our detection limit and C16-C36 were readily measured in SOM samples. There was no statistical difference between the total mass of PAH and alkanes quantified in this study (p=0.1). Weathering ratios computed for 3-ring PAHs indicated that only 5 of the samples demonstrated weathering (>20%) for alkylated phenanthrenes while alkylated dibenzothiophenes were similarly weathered (6/17). By weight SOMs are mostly composed of inorganics (52±17%), with oil components accounting for approximately 16±8% and the shells and plant matter accounting for 14±13% and 3.5±4% respectively. Carbon to nitrogen ratio (65 to 332) was above the optimum biodegradation range (less than 100) for 80% of the samples analyzed in this study. Data represent the first composition and weathering information on SOMs 2-3 years after the spill.

Factors Controlling Biodegradation of Buried MC252 Oil on a Coastal Headland Beach

L. Fitch, Z. Romaine, V. Elango, J. Pardue
Louisiana State University, Baton Rouge, LA

Since 2011, over 60% of oiled material removed during cleanup activities in the Gulf were removed from Fourchon Beach, Louisiana, a 9-mile coastal headland beach. Efforts to protect sensitive marsh areas using hard structures on these beaches created conditions for accumulation and burial of significant quantities of oil across the beach profile. Oil persists in these areas due to the natural anaerobic conditions of tidal groundwater on these beaches. The objectives of these field and laboratory studies are to determine factors controlling the rate and extent of biodegradation of 3-ring PAHs in crude oil trapped in the subsurface. In field samples, the ratio of total PAHs/C30 hopane ranged from 24 to 634 with lowest values were observed in SRBs from the surface where O2 limitations are absent. In the samples removed from depth, total PAHs/C30 hopane was significantly higher coincident with submergence in anaerobic groundwater. In the groundwater, high levels of sulfate (400 to 1500 mg/L) and sulfide (0.1 to 4 mg/L) were measured coupled with non-detectable dissolved oxygen (less than 0.02 mg/L). Groundwater pH is close to neutral, alkalinity ranged from 750 to 1400 mg/L, with ammonia and phosphate levels greater than 1.0 mg/L, suggests nutrient conditions favorable for biodegradation in the subsurface. However, persistence of alkylated forms of phenanthrenes, dibenzothiophenes and chrysenes even 4 years after the spill, suggests that biodegradation rates at the site under sulfate reducing conditions are too slow to serve as an effective natural recovery process. Additional laboratory studies using oiled sand and groundwater from the study site are in progress to evaluate if aerobic conditions would enhance biodegradation rates.

Examining Weathered Oil in Surface Residual Oil Balls from 2012-2014

H. K. White, **C. Wang**
Haverford College, Haverford, PA

Surface residual oil balls (SRBs) from the Deepwater Horizon oil spill were collected from beaches along the impacted coastline of the United States over a 3-year period from 2012 to 2014. GC-FID, FT-IR, and TLC-FID reveal compositional variability despite significant weathering in all samples. Higher percentages of polar compounds including oxygenated hydrocarbons correspond with lower percentages of saturates within all samples. The large volume of data also reveals subtle changes by year. GC-FID and TLC-FID indicate decreased proportions of saturates in samples collected at later dates with respect to the spill, independent of collection site. This decrease is associated with an increase in both oxygenated

and unsaturated compounds, as evidenced by TLC-FID and FT-IR. The maximum quantity observed for the polar fraction of oil is consistent for all three years, suggesting a stabilization and recalcitrance of oxygenated oil compounds. FT-IR is most useful in comparing the presence of oxygenated compounds and compositional changes within samples. Of the employed techniques, TLC-FID has demonstrated the greatest utility in SRB analysis, as it is the most quantitative and allows for comparison of all samples.

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

Mechanically Strong Aerogel Fabrics for Oil Capture and Recovery

O. Karatum[1], S. A. Steiner III[2], D. L. Plata[3]
[1]Duke University, Durham, NC, [2]Aerogel Technologies LLC, Boston, MA, [3]Yale University, New Haven, CT

Nearly 31 years separate the two largest oil spills in US History (Ixtoc I blowout June 1979; Macondo blowout April 2010), yet the responses to both disasters were nearly identical. In particular, efforts to keep oil from near-shore environments using booms and sorbents did not comprehensively retain oil and required manual deployment and recovery, creating unnecessary exposure for the workforce. Here, we explore the use of mechanically strong, ultra low density (0.1-0.15 g/cm), highly porous (80-99%), hydrophobic, flexible aerogel composite blankets as sorbent materials for oil capture and recovery. These two types of aerogels, Cabot™ Thermal Wrap® (TW) and Spaceloft® (SL), can be autofactured in a continuous geometry and rolled out as protective barriers in coastal environments and subsequently reclaimed with minimal intervention. Uptake of crude oils (Iraq and Bryan Mound Sweet) was 8.0 ± 0.1 and 6.5 ± 0.3 g/g for SL and 14.0 ± 0.1 and 12.2 ± 0.1 g/g for TW, respectively, nearly twice as high as similar polyurethane devices. Using chemical extraction, oil recoveries were 95 ± 2 (SL) and 90 ± 2% (TW), but this is an undesirable extraction route in decentralized oil clean up and from a waste perspective (e.g., ca. 1.2 L of solvent per g oil). In contrast, mechanical extraction routes are favorable, and a modest compression force (38 N) yielded 42.0 ± 0.4% over 10 reuse cycles for SL and 55.0 ±0.1% for TW initially, degrading to 30.0 ± 0.2% by the end of 10 cycles. Chemical-specific sorption on a surface area basis indicated that TW and SL are chemically similar, but physically and mechanically distinct: TW had the highest uptake and recovery for single-use applications, whereas SL performed best for multi-cycle reuse and recovery applications.

Assessing the Vulnerability and Implications of Modeled Oil Spills in the Gulf of Mexico

J. R. Nelson, L. Sim, J. Bauer, L. Romeo, K. Rose
National Energy Technology Laboratory, Albany, OR

Increasing interest in offshore hydrocarbon exploration, particularly in the deep and ultra-deep waters of the Gulf of Mexico, has highlighted gaps in both our knowledge and assumptions about the system. Some of these gaps were identified as a result of the 2010 Deepwater Horizon spill event which caused major ramifications for coastal communities surrounding the Gulf of Mexico. To further our understanding of the possible risks that may plague coastal communities in the wake of an uncontrolled hydrocarbon release event while assisting with prevention of future hydrocarbon spills, a spatial analytical approach has been developed to help inform all stakeholders and improve decision making

both in support of spill prevention as well as spill response and planning. To test this approach, a case study was performed in the Gulf of Mexico using a novel new oil spill blowout simulator, NETL's Blowout and Spill Occurrence Model (BLOSOM). Hypothetical spills were simulated each with a unique depth and spatial location. Data used in this scenario demonstrate how the approach can be used to determine vulnerability based on integration of socioeconomic data and environmental data describing the sensitivity of coastal environments to the effects of oil. In addition, hotel data and tourism information was incorporated for a better-rounded and informed analysis. Ultimately, this approach seeks to improve decision making by industry, regulators, and other entities to assist in spill prevention, but is also useful to stakeholders for response and planning needs. Finally, the approach demonstrated here is flexible and can be made more powerful by incorporating ecosystem services and data collected at the local level.

Lessons Learned Adapting NETL's Gulf of Mexico Integrated Assessment Model for other U.S. Regions

J. R. Bauer[1], J. Nelson[1], L. Sim[1], L. Romeo[1], T. Khangaonkar[2], A. Bunn[3]
[1]National Energy Technology Laboratory, Albany, OR, [2]Pacific Northwest National Laboratory, Seattle, WA, [3]Pacific Northwest National Laboratory, Richland, WA

Research gaps identified following natural and anthropogenic events in the Gulf of Mexico, such as Hurricanes Katrina and Rita as well as the Deepwater Horizon, prompted NETL to begin developing a full system (spanning the subsurface, wellbore, and water column) integrated risk assessment model (IAM). Focused primarily on oil spill prevention, efforts have sought to aggregate and integrate authoritative datasets into a suite of tools developed to model the fate and transport of deepwater blowouts, analyze the spatio-temporal patterns of modeled blowout scenarios, and assess the severity of those scenarios on different environmental factors and socio-economic activities within the Gulf of Mexico. Now, three years into the effort, we've begun expanding the capabilities of the models and analytical methods developed for the Gulf of Mexico for other regions in the U.S. as part of a multiple agency collaboration to evaluate worst case spill scenarios, environmental, social, and economic impacts, and spill response preparedness. Here, we present our efforts and some of the lessons learned in regards to adapting our models and approaches for different regions, including the offshore U.S. Arctic.

Using Oil Core Qualities for Predicting Dispersion of Spilled Surface Oil

M. Zeinstra-Helfrich[1,2], W. Koops[1], A. J. Murk[2,3]
[1]NHL University of Applied Sciences, Leeuwarden, Netherlands, [2]Wageningen University, part of Wageningen UR, Wageningen, Netherlands, [3]IMARES, Part of Wageningen UR, Den Helder, Netherlands

It is well agreed upon that it is hard to decide about application of oil spill dispersants or not, due to the trade-off between less oil on the water surface or in the water column. Knowing the flux (or rate) of natural and chemical dispersion of surface oil is crucial in estimating the (net) effects of chemical dispersion on the marine environment in a given situation. A spill response decision tool should be developed for use in "peace time" for response preparedness as well as during an actual spill situation for decision making. Required input parameters for such a tool should be readily available to oil spill responders through measurement, database retrieval and/or interpolation with other data.Our work aims to predict the consequences of oil type on the dispersion processes, in which oil type is described in a combination of physical properties (density, viscosity and oil-seawater interfacial tension). These

properties could be taken from an oil properties database or by on-scene measurement, possibly combined with an oil-weathering model. We investigate the relationship between oil type and properties on entrainment rate using the plunging jet test in which water is plunged upon an oil layer on water in a standardized way. The volume of oil entrained is quantified using image analysis. We aim to relate entrainment rate to the physical properties of the oil, to be able to extend current fate models.

Remote Sensing Systems for Oil Spill Detection and Analysis - A State of the Art Assessment

D. M. Burrage, S. C. Gallegos, J. C. Wesson, R. W. Gould Jr., S. C. McCarthy
Naval Research Lab, Stennis Space Center, MS

Efficient and rapid detection of oil spills occurring over the continental shelf is vitally important for many societal, environmental, economic and public safety reasons. The variety of spill sizes and types, coupled with the dynamic environment and rapidly evolving physical and chemical characteristics of a spill and changing weather conditions, makes detection and analysis using remote sensing methods challenging. At the same time, remote sensing technologies applicable to oil spills are steadily evolving. We describe the status and preliminary findings of a BSEE-funded project that is assessing the current capabilities and limitations of oil spill detection and analysis systems for use in offshore oil and gas operations on the US outer continental shelf. The assessment is motivated by the need for oil spill response planners and operators to access up-to-date information on State-of-the-Art oil spill remote sensing technologies. The work is based on recent experience with previous spills, such as the DWH spill, and the known performance of established and emerging remote sensing technologies. A set of oil spill scenarios and technology assessment criteria are proposed. Against the criteria, the efficacy and practicality of selected optical, infrared and microwave systems for use under different oil spill scenarios are being assessed. We present example assessments of selected sensor technologies and capabilities. A comprehensive set of such assessments will be stored in an evolving searchable and updateable web database with a graphical user interface, for future use by oil spill response and analysis professionals.

Commercial Satellite Radar Observations of the Deepwater Horizon Oil Spill

M. Caruso, J. Hargrove, H. Graber
University of Miami, Miami, FL

An unprecedented amount of resources were expended monitoring the fate of oil discharged during the Deepwater Horizon (DWH) oil spill. One aspect of this effort was the use remote sensing to monitor the extent and movement of oil at the sea surface. Satellite data were downlinked and processed at the Center for Southeastern Tropical Advanced Remote Sensing in Miami. The data and analyses were disseminated within one hour of acquisition. More than 1400 images spanning the Gulf of Mexico from Texas to Florida were analyzed and distributed to federal and state agencies. Commercial satellite synthetic aperture radar (SAR) data were used to identify the full surface extent of the oil due to its day/night ability to observe large areas of the sea surface in all weather conditions. There were many lessons learned from the remote sensing aspect of the response. Commercial SAR is a practical tool for identifying oil spills and planning effective resource allocation across the Gulf of Mexico as well as in coastal estuaries. Although automated detection techniques provide rapid analysis of imagery, expert analysts are vital for assessing conditions and communicating with OSCs. Since oil spills are extremely dynamic, any delay in delay in dissemination of remote sensing analysis will reduce the usefulness of the

information. If satellite SAR data are used in an oil spill situational awareness program that integrates environmental observations and high resolution numerical models, OSCs could be provided with knowledge essential for effective asset allocation. Additionally, feedback from OSCs would give satellite planners the ability to target specific areas to facilitate containment or mitigation efforts.

Detection of Oil Thickness Signatures in Synthetic Aperture Radar (SAR) and Hyperspectral Satellite Imagery

O. Garcia Pineda[1], G. Staples[2], K. Bannerman[2], I. MacDonald[3]
[1]Water Mapping, Tallahassee, FL, [2]MDA Corporation, Vancouver, BC, Canada, [3]Florida State University, Tallahassee, FL

Monitoring oil spills with remote sensing is a well-established technique. Recently, by combining hyperspectral and microwave satellite images collected during Deepwater Horizon spill, we have learned that features associated with oil emulsions can be detected with synthetic aperture radar (SAR) and optical-infrared sensors. This is of great importance because during oil spill events thick patches of hydrocarbons are highly toxic for the marine environment, and it is these patches of thick oil that can be most effectively recovered or treated during response operations by burning, skimming, or use of aerial dispersants. In this project, we present our ongoing work and our latest results, including the development of an algorithm that delineates thick oil signatures in satellite imagery. This technique is validated in a recent field campaign, where oil samples were collected (over the Energy Taylor oil spill area in the Gulf of Mexico). The chemical and spectral properties of oil samples recovered in the field are used to fingerprint their signatures in the satellite imagery. Oil emulsion features were identified in Quad-polarimetric SAR imagery collected by RADARSAT-2 and hyperspectral imagery collected by EO-1 and Hyperion. The viscoelastic (surface roughness) and dielectric (conductivity) properties of oil emulsions seem to be the main factor for the detection of these features on SAR imagery. Our results have demonstrated the importance of remote sensing support for detecting oil spills and the potential use of SAR imagery to detect floating thick oil emulsions.

Future Autonomous Underwater Vehicle Adaptive Sampling on the Mississippi-Alabama Shelf

T. Miles[1], O. Schofield[2]
[1]Department of Marine and Coastal Sciences, Center for Ocean Observing Leadership, New Brunswick, NJ, [2]Center for Ocean Observing Leadership, New Brunswick, NJ

As part of the CONsortium for oil spill exposure pathways in Coastal River-Dominated Ecosystems (CONCORDE) project we will be deploying a suite of autonomous underwater vehicles on the Mississippi-Alabama shelf in 2015 and 2016. These underwater glider deployments, along with other observational assets, will be used to characterize the physical, geochemical, and bio-optical fields influenced by pulsed river discharge and identify the 3-D pathways of oil/disperants to the coast. The glider assets will be used to guide ship-based surveys of plankton (phyto and zooplankton) as well as develop an adaptive sampling framework within regional models, where models suggest regions of interest to sample, gliders investigate and then feed data back to models to improve overall simulation. This format will leverage heavily from past large-scale glider networks such as GliderPalooza in 2013 & 2014 and ONR/NSF sponsored adaptive sampling exercises in 2009. Additionally, these glider assets will be staged for rapid response deployments in the event of an oil spill similar to glider activities following

the 2010 Deepwater Horizon oil spill, and also in response to impending storm events such as Hurricane Sandy and Arthur as in the CINAR Tempests project on the Mid-Atlantic Bight.

Regeneration and Characterization of Silica Aerogels: Implications for Oil Spill Clean-Up

Y. Hu, **C. Zhang**, C. Dai
University of Houston, Houston, TX

Silica aerogel, a porous hydrophobic adsorbent, has widely been used for oil spill clean-up due to its high adsorption capacity. In this study, the adsorption capacity (mass of oil adsorbed per unit mass of silica aerogel) on toluene, petrol, or diesel was determined by weighting the mass difference before and after adsorption. The adsorption capacity of toluene, petrol and diesel on silica aerogels were measured to be 12.03, 11.07, and 12.43 g/g, respectively. Successful adsorption of toluene, petrol, or diesel on silica aerogel was confirmed by Fourier transform infrared spectra (FTIR), where C-H bonds can be explicitly detected. Desorption of previously saturated silica aerogels was investigated by thermal treatment (80°C for toluene and petrol, or 200°C for disel). Based on mass measurements, toluene and petrol were completely desorbed from silica aerogels, while ~ 6% diesel remained on silica aerogels. The mass measurements were consistent with FTIR measurements: C-H bonds were not detected for silica aerogels after desorption of toluene, while weak signals of C-H bonds were detected for that of petrol and diesel. After desorption, the adsorption capacities of regenerated silica aerogels were measured, and were found to have decreased by ~ 5.0% for toluene, ~35.5% for petrol, and ~88.4% for diesel. As the porous structures of silica aerogels contribute greatly to their high adsorption capacity, to elucidate the mechanisms of their adsorption capacity decrease after regeneration, the pore sizes of silica aerogels after regeneration were measured by small angle X-ray Scattering (SAXS). SAXS results showed that the decrease in pore sizes after regeneration were consistent with the decrease in adsorption capacity: for silica aerogel with the original average pore size of 20 nm, after adsorption and desorption, the average pore size decreased to 14.6 nm for toluene, to 13.6 nm for petrol. While for diesel, no significant amounts of pores were detected after regeneration. Our results indicated that the collapse of the porous structure was the reason for the adsorption capacity decrease after regeneration. This study provided new sight on the regeneration of silica aerogel for oil spill clean-up, which may help to develop an economic treatment approach.

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

Inorganic Carbon and pH in the Gulf of Mexico: Understanding the Deepwater Horizon Region

J**. Young**[1], S. Yvon-Lewis[1], T. S. Bianchi[2], M. Shields[2], M. Du[1]
[1]Texas A & M, College Station, TX, [2]University of Florida, Gainesville, FL

The breakdown and respiration of oil compounds may contribute to the dissolved inorganic carbon (DIC) pool and thus ocean acidification. The Gulf of Mexico (GOM) has an abundance of natural seeps as well

as numerous manmade structures that could provide a source of hydrocarbons to the water column. Samples of seawater were collected on the first GISR (Gulf Integrated Spill Research) cruise (G01) during the first week of July 2012. This cruise covered an area of ~1360 km2 roughly centered on the site of the Deepwater Horizon disaster. Alkalinity profiles for the southeastern most stations indicate lower (~100 µmol/kg) alkalinities at depth when compared to other stations. This results in calculated pHs that are ~0.5 units lower at depth than they are at the other stations. Another group of stations show increased DIC concentrations on the order of 100-150 µmol/kg higher than average at depths around 800 m and 1200 m leading to calculated pHs about 0.2to 0.4 below average for those depths. These features may or may not be persistent in this region, and the elevated DIC concentrations may relate to organic matter (petroleum or other) oxidation. Samples were collected from this same region 2 years later (June 2014). The persistence of these features will be discussed and an assessment of the organic carbon respiration contribution to the lower pHs will be presented.

Changes between 2008-2011 in Seasonal Average Trace Metal Concentrations in Bottom Sediment Retrieved from the Eastern Outer Continental Shelf (OCS), Gulf of Mexico

D. Steffy, A. Nichols, J. Morgan
Jacksonville State University, Jacksonville, AL

Higher nickel, vanadium, and lead concentrations measured in sea bottom sediment of the eastern OCS can be explained by the presence of a new source for these metals from the damaged Mconco Well which resulted in the BP Deepwater Horizon Oil Spill during the spring of 2010. Fifty-seven sediment samples were collected during the fall months for the years 2008-2011 from the eastern OCS. The Tukey range test was used to compare six metal concentrations between the relict sand deposits of the northern Gulf OCS to the relict carbonate sediments off of western Florida OCS. Tests indicated that nickel, vanadium, and lead were significantly higher ($p < 0.05$) in the seasonal average concentrations in the relict sand deposits. These higher concentrations are also reflected in the vanadium to nickel ratio being statistically different ($p < 0.005$) for carbonate sediment (1.70 ± 0.24) when compared to relict sand (0.96 ± 0.12) in the north, which is closer to the damaged well. This difference indicates a new source of nickel that accumulated through time in the north. In the carbonate sediment there appears a zonation of the ratios with a dependency on water depth. The V/Ni ratio is 0.80 ± 0.10 for samples taken in water depths at or deeper than 200 m; and ratios are 2.06 ± 0.42 for samples taken in water depths shallower than 200 m.

Temporal Trends of Florescence Estimated Oil Equivalents in the Water Column during and Four Year after the Deepwater Horizon Spill

T. L. Wade, S. T. Sweet, J. L. Sericano, D. Shi, N. L. Guinasso, Jr
Texas A&M University, College Station, TX

Total scanning fluorescence (TSF) is an effective screening tool to detect the presence of aromatic compounds derived from petroleum in environmental samples. TSF analyses was done to provide estimated oil equivalents (EOE) for 958 discreet water samples collected at various depths throughout the water column. The range of EOE for the 294 samples collected during the release was < 0.7 to 440 ug/L. The range of concentrations for the 664 samples collected between July 2012 to June 2014 was

<0.07 to 28 when the one surface sample in an observed surface slick (3800 ug/L) is not included. Sources of hydrocarbons in the water column include spills, natural seepage, oil production activities, ship activities, coastal run-off and atmospheric deposition. Selected samples analyzed for polycyclic aromatic hydrocarbons (PAH) during the spill confirmed the presence of petroleum in samples with elevated TSF. Other samples PAH analyses for samples collected in the vicinity of the Loop Current during the spill indicating mixed sources that were not fresh DWH oil. Water samples collected in the vicinity of the Loop Current during the spill and after four years after the spill had low EOE and PAH concentrations. The PAH distribution indicates mixed sources.

Spatial and Temporal Comparison of Pre- and Post- Deepwater Horizon Spill Hydrocarbon Records in Sediments from the Gulf of Mexico

J. R. Radović, R. Correa Silva, G. Gonzalez Arismendi, A. Jaggi, R. Snowdon, P. Weerawardhena, S. R. Larter, T. B. P. Oldenburg
University of Calgary, Calgary, AB, Canada

The Gulf of Mexico (GoM) receives significant oil inputs from both natural sources (oil seeps) and anthropogenic activity (offshore oil production). The Deepwater Horizon (DWH) platform disaster in 2010 led to unprecedented underwater release of oil from the Macondo well into the GoM. Only a portion of the spilled oil was recovered, leaving the majority of oil in the environment. In addition, large quantities of dispersants were, for the first time, applied subsurface, in order to retain the oil in the deep water, and minimise surface slick effects. Therefore, a mixture of oil components, dispersants and oil-flocculent material from the spill might have accumulated in the offshore sediments. In order to investigate this, pre- and post- DWH hydrocarbon records in the recent GoM sediments were compared. To this end, sediment samples were collected in the period from December 2010 to August 2014, from near the oil spill area and from more distant locations around the spill site, extracted, and analyzed by conventional methods (e.g. GC-MS) as well as the state of the art techniques such as FTICR-MS. FTICR-MS is better suited for detection and analysis of non-hydrocarbon species, including dispersant chemicals and any polar alteration products. From these results, temporal and spatial hydrocarbon trends in the analyzed sediments were derived and the contribution of the DWH spill inputs and added chemicals was estimated and will be presented.

Constraining the spatial extent of the Marine Oil Snow Sedimentation and Accumulation (MOSSFA) following the DWH Event using a 210Pb inventory Approach

P. Schwing[1], G. R. Brooks[2], R. A. Larson[2], C. W. Holmes[3], B. J. O'Malley[1], D. J. Hollander[1]
[1]University of South Florida, Saint Petersburg, FL, [2]Eckerd College, Saint Petersburg, FL, [3]Environchron, Bradenton, FL

Following the Deepwater Horizon (DWH) event in 2010, there were several lines of evidence indicating that a significant amount of marine oil snow was formed at the surface of the Gulf of Mexico (GoM). The marine oil snow settled quickly through the water column and ultimately accumulated in the sediments of the northern GoM (MOSSFA event). A series of sediment cores throughout the northern GoM were collected from 2010-2014 to determine the spatial and temporal extent of this MOSSFA event. This study utilized sedimentary inventories of a commonly used radioisotope tracer (210Pb) to characterize

the spatial expression of the MOSSFA event on the seafloor. 210Pb inventories document spatial and temporal changes in sedimentation patterns in the aftermath of the DWH event. Relative to pre-DWH conditions, changes in sedimentary regime occurred in two distinct regions: 1) an area centered on the DWH wellhead extending ~50 NM on the continental slope (500-1000 m water depth) along a southwest-northeast trajectory and 2) the area of the DeSoto Canyon extending ~45-60 NM to the northeast of the DWH wellhead along the continental slope (400-1000 m water depth). Continued evaluation of 210Pb inventories will provide a valuable tool in documenting the ongoing spatial extent of the MOSSFA pulse following the DWH event and will continue to aid in the determination of advective/cross-shelf transport and ultimate depocenters of the oiled-flocculent material.

Transience and Persistence of Natural Hydrocarbon Seepage in Mississippi Canyon, Gulf of Mexico

O. M. Garcia Pineda[1], I. MacDonald[2], W. Shedd[3], M. Silva[2]
[1]Water Mapping, Tallahassee, FL, [2]Florida State University, Tallahassee, FL, [3]BOEM, New Orleans, LA

Analysis of the magnitude of oil discharge from natural hydrocarbon seeps will improve understanding of the carbon cycle and the Gulf of Mexico (GOM) ecosystem. With use of a large archive of remote sensing data, in combination with geophysical and multibeam data, we identified, mapped, and characterized natural hydrocarbon seeps in the Macondo prospect region near the wreck site of the drill rig Deepwater Horizon. Satellite image processing and cluster analysis revealed locations of previously undetected seep zones (SZ). A total of 562 individual gas plumes were also detected in multibeam surveys. In total, SAR imagery confirmed 52 oil-producing SZ in the study area. In almost all cases gas plumes were associated with oil-producing SZ. The cluster of seeps in the vicinity of lease block MC302 appeared to host the most persistent and prolific oil vents. Oil slicks and gas plumes observed over the DWH site were consistent with discharges of residual oil from the wreckage. In contrast with highly persistent oil seeps observed in the Green Canyon and Garden Banks lease areas, the seeps in the vicinity of Macondo Prospect were intermittent. The quantity of surface oil detected in Green Canyon was almost two orders of magnitude greater than in Mississippi Canyon.

Changes in Sedimentary Barium following the BP DWH Blowout Event

T. Bartlett[1], D. W. Hastings[1], G. R. Brooks[1], B. Carr[1], C. Selden[1], K. A. Quinn[2], D. J. Hollander[2]
[1]Eckerd College, St. Petersburg, FL, [2]University of South Florida, St. Petersburg, FL

After the Deepwater Horizon blowout event, there was a pulse in sedimentation rate, which was caused by mucous rich marine snow associated with fine grained clay sized minerals. Sediment cores were collected in the NE Gulf of Mexico from August 2010 to August 2014. Barium (Ba) is controlled by several factors and processes that could have contributed to changing concentrations. The main controls for barium include drilling muds, cold seeps, and changes in overlying primary production. Drilling muds contain powdered barite (BaSO4), a very dense mineral often used to prevent oil from escaping the hole during drilling processes. Barite forms at cold seeps, which are abundant in the northern Gulf of Mexico. Diagenetic processes also contribute to elevated barium levels. Sediments were sampled at high resolution (2 mm), microwave digested in concentrated nitric acid at high temperature and pressure, followed by analysis via ICP-MS. From these data it has been found that barium levels range from 200ppm, an apparent background level, to over 1500ppm. We will constrain different processes that

control changing barium concentrations in sediments in the northern Gulf of Mexico following the blowout event.

Utilizing the Sedimentary Record of Planktonic Foraminiferal Accumulation Rates to Validate Surficial Marine Oil Snow Flux following the Deepwater Horizon Event

H. M. Ramirez[1], P. Schwing[2], D. Hastings[1], A. Larson[1,2], G. Brooks[1], D. Hollander[2]
[1]Eckerd College, St. Petersburg, FL, [2]USF Marine Science Lab, St. Petersburg, FL

Several lines of evidence, including water column and sedimentary measurements, have suggested that Marine Oil Snow Sedimentation and Flocculent Accumulation (MOSSFA) increased dramatically in the northern Gulf of Mexico (GoM) following the Deepwater Horizon (DWH) event. However, except for molecular organic geochemical indicators (genomics 16S and lipid biomarkers of photoautotrophs and pyrogenic PAHs of hydrocarbon origins) few of those records confirm that the material that reached the sediments was necessarily from the surface (or near-surface) of the water column. This study identifies the abundance and accumulation rates of planktonic foraminifera (consumer organisms which live in the upper 100 m of the water column) to determine what proportion of MOSSFA inputs originated in the surface waters. Accumulation rates were determined based on short-lived radionuclide geochronologies: 210Pb, 234Th. Sediment cores were collect from two sites, PCB06 and DSH08, on four consecutive research cruises from December 2010 to August 2012. Preliminary results suggest a 2 to 4 fold increase in both abundance and accumulation rate in the top 10 mm of sediment relative to background (down-core), consistent with the post-DWH impacted layer. Such an increase in planktonic foramnifera abundance provides an independent line of evidence for MOSSFA processes and confirms that the organic and inorganic material which originated in the upper 100 m of the water column were aggregated and deposited in the sediments.

Distribution and Accumulation of Polycyclic Aromatic Hydrocarbons in the Northern Gulf of Mexico Sediments

P. L. Adhikari, K. Maiti, E. B. Overton
Louisiana State University, Baton Rouge, LA

Deep-sea sediments are considered to be the global sink of persistent organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) released into the marine ecosystems via different sources. Seventeen sediment cores were collected from the northern Gulf of Mexico (GOM) in between 2011 and 2013, including 5 cores collected around Deepwater Horizon (DWH) spill site, and analyzed for PAHs. The sediment PAHs concentrations of forty three 2-6 ring PAHs (∑PAH43) varied between 12 to 187 ng/g of dry weight in the top 5 cm of the sediments. These values are within the range of pre-spill PAHs concentrations previously reported from this region. The PAHs accumulation rates calculated by combining PAHs concentrations and 210Pb based sedimentation rates varied between 2 to 64 ng/cm2/yr. The coastal stations had significantly higher PAHs concentrations and accumulation rates than the deeper stations (P-value <0.01). Recent/surface sediments were elevated (P-value <0.01) in PAHs concentrations and accumulation rates than the underlying sediments, however the changes were more pronounced in deep-sea sediments, possibly due to DWH oil inputs. Lower molecular weight (2-3 rings) PAHs and alkyl homologous dominated the PAHs profiles in all the sediment cores indicating petroleum contaminations as a major source of PAHs in this region however, the source diagnostic ratios of PAHs isomers and principal component analysis suggested mixed sources.

Sedimentary Record of PAHs in Offshore Areas of the Northern Gulf of Mexico after the Deepwater Horizon Oil Spill

Q. Miller[1], I. C. Romero[1], G. R. Brooks[2], R. A. Larson[2], P. Schwing[1], D. Hollander[1]
[1]University of South Florida St. Petersburg, Saint Petersburg, FL, [2]Eckerd College, Saint Petersburg, FL

In 2010, the Deepwater Horizon (DWH) oil rig exploded discharging 4.9 million barrels of oil across the Gulf of Mexico (GoM). Preliminary evidence of widespread sedimentary oil deposition warranted further research. Sediment cores were collected at five sites along the continental shelf/slope and sectioned samples were analyzed for polycyclic aromatic hydrocarbons (PAH). Short-lived radioisotopes were used to develop core chronologies. Here we document variable PAH content and composition, throughout the sedimentary record reflecting both background and oil-derived inputs. The site closest to the Mississippi Delta (~50 km) had the highest concentrations of background PAH inputs (1223 ng/g), with concentrations decreasing as distance from the delta increased. Elevated levels of PAHs in the surficial records along the continental slope indicate exposure to the DWH event. In the 2010 sample layer taken close to the DWH wellhead, PAH concentrations were 10 times that of the background mean. The increase in high molecular weight PAHs provides evidence for a deposition event of surface-water particles occurring during the blowout. In contrast, a site located 118 km SW of the wellhead is dominated by low molecular weight PAHs, indicating impingement of sub-surface plumes at a depth of ~1100 m. These results provide insight into the spatial distribution of sediment PAH concentrations and the mechanisms of deposition following the DWH event.

Temporal Variability in Total Oxygen Utilization by Hydrocarbon-Rich Sediments at Lease Block MC118, Northern Gulf of Mexico

C. S. Martens[1], H. Mendlovitz[1], H. Seim[1], L. Lapham[2], M. D'Emidio[3]
[1]UNC-Chapel Hill, Chapel Hill, NC, [2]University of Maryland, Solomons, MD, [3]University of Mississippi, University, MS

Sediment Total Oxygen Utilization (TOU) rates were estimated from continuous, in situ current and optode oxygen sensor measurements at two sites at 832-834 m depth in lease block MC118 in the northern Gulf for 21 to 160-day periods utilizing a multi-sensor-open chamber system deployed by benthic lander. Temporal variability in current direction and speed and water temperature revealed strong influences of bathymetrically steered currents and overlying, along-shelf flows on local and regional water transport processes. Dissolved Oxygen (DO) concentrations and temperature were inversely correlated as a result of water mass mixing processes. TOU was estimated as the product of an eddy diffusivity K and the gradient of DO within the chimney $F = K (\Delta DO/\Delta z)$. Calculated eddy diffusivities and TOU had means of 3.96x10-4 m2/s and 11.6 mmol/(m2day) during the 160-day deployment, within the observed range of TOU for upper slope environments. The observed TOU values can be attributed to the high benthic activity that characterizes the MC118 area including active hydrocarbon seeps, high rates of biogenic methane production and high densities of bacterial mats. Flux chamber DO concentrations measured during the 21-day deployment exhibited quasi-daily variations apparently resulting from an interaction between near inertial waves and the steep topography of an elevated scarp immediately adjacent to the 21-day deployment site that modulated currents at the top of the open chamber. A combination of continuous current velocity and oxygen optode concentration gradient measurements within open cylinder chambers allows estimation of TOU for sustained periods in the deep sea using methodology available to many deep-sea researchers.

Projection of the Deepwater Horizon Spill in the Gulf of Mexico Water Column Using Biogeochemical Tracers

J. Kolasinski, B. E. Rosenheim
University of South Florida, St Petersburg, FL

The Deepwater Horizon rig explosion and subsequent leak of the Macondo Well in the Gulf of Mexico (GOM) released crude oil composed of a variety of hydrocarbon compounds at depth (1500m). This resulted in both a surface and sub-surface (1000-1300 m) oil-concentrated plumes. The surrounding oceanic region is highly dynamic with open GOM waters interacting with both riverine waters of the Mississippi-Atchafalaya system and the Loop Current, producing strong surface and sub-surface physical and chemical gradients (i.e. salinity). However, the source and fate of carbon are poorly understood in this region despite being a prerequisite to interpretations of the presence and transformation of oil-derived carbon in the pelagic ecosystem, particularly since oil is no longer recognizable using traditional analysis (e.g. PAHs). Three oceanographic campaigns were conducted in 2012, 2013 and 2014. We used a combination of biogeochemical and isotopic tracers (i.e. [DIC], δ13C, Δ14C) to (1) give new insights to the carbon cycle in relation to oceanographic and coastal processes in the northern GOM and (2) to investigate the incorporation of oil in the different carbon pools (particulate and dissolved, organic and inorganic, methane). We will discuss changes in the DIC concentrations at the deep plume depths without accompanying isotopic changes as well as the isotopic effects of the Mississippi-Atchafalaya plume on surface carbon cycling.

Recent Sedimentation in the Southern Gulf of Mexico

J. A. Sanchez-Cabeza, A. C. Ruiz-Fernández, M. L. Machain-Castillo, L. H. Pérez-Bernal
Universidad Nacional Autonoma de Mexico, Ciudad de Mexico, Mexico

Sedimentary records are useful tools to reconstruct environmental changes in the Oceans. In order to study the recent sedimentation processes in a large region of the Southern Gulf of Mexico, we collected 23 box-cores from depths ranging from 249 to 1785 m. Cores were analyzed for 210Pb, through 210Po in secular equilibrium, by using high-resolution alpha spectrometry and recent mean sediment (SAR) and mass (MAR) accumulation rates were determined by using the Constant Flux Constant Sedimentation (CFCS) 210Pb dating model. Accumulation rates showed a 5-6 fold variation range: SARs ranged from 0.48 to 2.61 (mean 1.0 ± 0.5) mm yr-1, and MARs ranged from 0.026 to 0.164 (mean 0.07 ± 0.03) g cm-2 yr-1. Based on geographical, geochemical and sedimentological parameters, the study region was sub-divided into 8 zones. The highest SARs were observed in a submarine delta (zone IA: 1.49 ± 0.01 mm yr-1), the closest area to the Coatzacoalcos river (zone VI: 1.45±0.08 mm yr-1), and the lowest in a plateau in the salt domes province (zone VII: 0.54 ± 0.09 mm yr-1). The geomorphological complexity of the region prevents a statistically significant correlation of SARs with depth. However, high SARs and 210Pb fluxes could be observed in deep stations, located in the distal part of the western slope.

Chemometric Characterization of Deep Water Sediments in the Southern Gulf of Mexico

A. C. Ruiz Fernandez[1], J. A. Sanchez-Cabeza[2], M. L. Machain-Castillo[2], D. Hastings[3], L. H. Perez-Bernal[1]
[1]UNAM, ICMyL- UA Mazatlan, Mazatlan, Mexico, [2]UNAM, ICMyL, Mexico City, Mexico, [3]Eckerd College, St. Petersburg, FL

The textural composition and the concentration of indicator elements commonly used to assess the terrigenous input (Al, Ti, Zr) and the redox conditions (Fe, Mn, Mo, V, Re) were studied in a 14 cm sediment core collected at 1,263 m depth from the Gulf of Mexico, to understand the influence of such factors on the distribution of metal pollutants associated to industrial sources in the surroundings, i.e. oil exploitation activities. The sediments were mostly silty (>85%), the clay content was usually <7%, except between 1 to 3 cm depth, where it increased up to 14% and maximum Fe, Mn and Mo concentrations were also observed. The sand fraction in this section is foraminiferal ooze. The Al and Ti concentration profiles were almost homogenous along the core, indicating a steady detrital composition. Most trace element depth distribution showed slight variations with undefined trends; and only As and Pb showed increasing concentrations from the bottom to the core surface. Through a Principal Component Analysis, it was found that Mn, Fe, Mo, As and Pb were closely related to the clay fraction; Zr, Zn, Co and sands were associated to the terrigenous input, and Re, Cr, Cu, Ni and V to the silt content. Our conclusion is that the scavenging of metals by Fe-Mn oxide coatings on clays and the adsorption or of trace elements onto clay mineral surfaces (grain-size effect) are important factors that must be taken into consideration when assessing trace metal pollution in the sediments.

Longitudinal Studies of Gulf of Alaska Samples by GCxGC and Chemometric Analysis

G. Hall[1], **A. Kloo**[1], **N. Morin**[1], C. Aeppli[2]
[1]U.S. Coast Guard Academy, New London, CT, [2]Bigelow Laboratory for Ocean Sciences, East Boothbay, ME

Samples from multiple locations in the Gulf of Alaska spanning 25 years were analyzed by GCxGC-FID. Observations of these samples have shown location and situation specific weathering dynamics and also biomarker changes, possibly due to the impact of subsequent petroleum exposure. Chemometric analysis including Partial Least Squares Regression (PLS), and PLS - Discriminant Analysis (PLS-DA) were applied to identify anomalous samples and the comprehensive scope of chemical changes in these samples. Additionally, all samples were identified on a "open weathering" timeline to describe the range of weathering dynamics occurring in the Gulf of Alaska. These findings have implications for the long term monitoring and fingerprinting of any present or future spill.

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

Predicting Long Term Impacts of Oil/Dispersant Exposures on Human Health and Higher Trophic Organisms: Obesogenicity

A. Temkin, R. Bowers, D. Spyropoulos
Medical University of South Carolina, Charleston, SC

Obesity is a global health epidemic implicated by many factors. Recently, exposures to environmental obesogens, chemicals that alter lipid homeostasis to promote obesity, have emerged as distinct contributing factors. Often these compounds increase fat cell differentiation via interaction with the nuclear hormone receptor PPARγ. Identification of obesogens is a critical step in reducing exposures and improving human health through preventative measures. Previous studies have indicated that components of crude oil may be potent obesogens. We have identified obesogenic fractions in Deepwater Horizon MC252 crude oil and Corexit EC9500 dispersant using PPARγ ligand binding receptor transactivation assays, demonstrating a high throughput assay for identification of PPARγ ligands in oil fractions. We detected the presence of PPARγ ligands in Corexit water accommodated fractions and Corexit only fractions. We further identified dioctyl sodium sulfuccinate, a surfactant component of Corexit, as one such obesogenic constituent. We have begun to validate these fractions for obesogenicity using in vitro and in vivo models. For in vitro studies, we are using quantitative live cell RNA detection probes to optimize both the dosage and timing of exposure to fractions and components. Under such optimized conditions, transcriptome analyses on human induced pluripotent stem cells and mesenchymal stem cells reveal common and unique patterns of gene expression change based on component tested. Similarly, future work will determine the mechanism by which Corexit containing fractions increase the obesogenic potential of MC252 oil to drive development of oil spill clean up measures with safer long-term health trajectory profiles.

Development of a Fish Liver Microtissue Model to Characterize the Toxicity of PAHs and Particle-Based Dispersants

A. L. Rodd, M. A. Creighton, R. H. Hurt, A. B. Kane
Brown University, Providence, RI

Fine particles can assemble at water-oil interfaces to stabilize oil droplets, forming what is known as a Pickering emulsion. Particle-based formulations are under development for use as dispersants following oil spills, and this project focuses on the potential impacts of environmental exposures to these particles on aquatic organisms like zooplankton and fish. The project's next phase will examine the environmental impacts of co-exposure to polycyclic aromatic hydrocarbons and surface-engineered carbon black as a model Pickering dispersant on marine vertebrates using a fish liver cell line, PLHC-1, in a three-dimensional (3D), scaffold-free microtissue model. 3D cultures can provide the benefits of in vivo-like cell-cell interactions and the opportunity for longer term cultures, but there are also challenges associated with imaging through thicker tissues, maintaining viability, and adapting monolayer toxicity assays to 3D systems. Assays to determine the toxicity of polycyclic aromatic hydrocarbons (PAHs) and nanoparticles, including oxidative stress and Cyp1a activity, will be optimized in monolayer and then adapted for use in 3D. To characterize the PLHC-1 liver spheroids, changes in viability, differentiation, and Cyp1a activity will be measured over long term cultures of spheroids. This research is supported by

BP/The Gulf of Mexico Research Initiative, NIEHS Training Grant T32 ES07272, and the generous support of Donna McGraw Weiss '89 and Jason Weiss.

A Quantitative Assessment of the Impact of Surfactant Stabilized Interfaces on the Growth of *Alcanivorax borkumensis*

M. Bookstaver[1], A. Bose[2], A. Tripathi[1]
[1]Brown University, Providence, RI, [2]University of Rhode Island, Kingston, RI

Alcanivorax borkumensis is a hydrocarbon degrading bacterium linked to oil degradation around oil spill sites. It is known to be a surface bacteria leading to substantial interaction with the oil water interface. Because of its prominence in oil spill regions, it has great potential to be used actively in oil spill remediation. Dispersants are thought to be important in the creation of oil in water emulsions that are meant to aid in the biodegradation process by bacteria. Although it is likely that some sort of dispersant will be used again in the case of another oil spill, to date, no studies have shown the impact of certain dispersants on the bacteria population. Corexit was the main dispersant used during the Deepwater Horizon oil spill, but little is known about its effect on the bacteria community. We use Dioctyl sulfosuccinate sodium salt, one of the components of Corexit, and L-α-Phosphatidylcholine, a natural emulsifier, to investigate the impact of dispersants on *Alcanivorax borkumensis*. Here we assess the impact of these two dispersants on the growth of *Alcanivorax borkumensis*. The results of this study are critical in the decision of dispersant use in the future. We also use *Alcanivorax borkumensis* to probe the difference in growth in the presence of difference carbon sources. We investigate the growth when in contact with dissolved organic carbon only (as is the case when there is no oil spill), octane (a short alkane), iso-octane (a simple branched alkane), and some combination of the two oils. We use these results to determine how we can better encourage the bioremediation of oil spills by bacteria like *Alcanivorax borkumensis* in the future.

Quantifying Hydrocarbon Toxicity to Shallow-Water Corals: Improving NEBA for Dispersant Decision-Making

D. A. Renegar[1], N. R. Turner[1], B. M. Riegl[1], R. E. Dodge[1], A. H. Knap[2], P. A. Schuler[3]
[1]Nova Southeastern University Oceanographic Center, Dania, FL, [2]Texas A&M University, College Station, TX, [3]Oil Spill Response USA Inc., Fort Lauderdale, FL

Shallow water coral reef ecosystems have an elevated chance of exposure to hydrocarbons due to their close proximity to the coastline. Previous research to evaluate hydrocarbon toxicity to corals and coral reefs has generally focused on community level effects, and results are often not comparable between studies. Thus, a significant data gap exists on the toxicity thresholds of hydrocarbons to corals, from the organismal to cellular level. Targeted hydrocarbon toxicity studies are therefore vital to accurate assessment of coral resilience to hydrocarbon exposures. To fill this need, the scope of this research includes a suite of experiments investigating hydrocarbon toxicity on the shallow water coral Porites divaricata. As constituent hydrocarbons in oil have additive effects, initial focus is development of a target lipid model, critical body burden based toxicity testing protocol for corals using 48-hour constant exposures with individual hydrocarbons. Acute and sub-acute effects (color, polyp extension/retraction, tissue loss/mortality, PAM fluorometry, and histologic cellular changes) will be assessed both during exposure and during a post-exposure recovery period. Subsequent experimentation will utilize additional single hydrocarbons and chemically enhanced water accommodated fractions (CEWAF) of

one oil-dispersant combination to refine model accuracy. The toxicity thresholds determined in this study will provide needed data for modeling impacts of potential hydrocarbon concentrations and exposures. This information can then be used in Net Environmental Benefit Analysis (NEBA) of predicted impacts and response methods in coral reef environments. Initial results of a three year study will be presented.

Monitoring of DOSS Hydrolysis Metabolites in Seafood Collected from the Gulf of Mexico

D. Sparks, C. Foster, A. Meredith
Mississippi State Chemical Laboratory, Mississippi State, MS

During the aftermath of the Deepwater Horizon oil spill, dispersants were used to help distribute the oil into the water. The main dispersant used during the clean-up was Corexit, with the primary active ingredient being dioctylsulfosuccinate (DOSS). Since the oil spill, the Mississippi State Chemical Laboratory has been monitoring DOSS levels in seafood samples collected by the Mississippi Department of Marine Resources. Recently, we began monitoring seafood for the hydrolysis product of DOSS using liquid chromatography with triple quadrupole mass spectrometry detection. The results presented here focus on levels of metabolite seen in various seafood types (crab, fish, oyster, and shrimp) in comparison to levels of DOSS also found within the same samples.

Combined Effects of Hypoxia and Dispersed Oil on Sheepshead Minnow Larvae

I. Huang, S. Dasgupta, A. McElroy
Stony Brook University, Stony Brook, NY

The Deepwater Horizon oil spill in 2010 resulted in the largest releases of oil and oil dispersants to date in the United States. It is likely that future oil and dispersed oil releases may occur in areas of the Gulf of Mexico where the additional stress of hypoxia is present. Seasonal hypoxia is now a common feature of the Northern Gulf, which is likely to increase in severity and reach with continuing anthropogenic nutrient inputs. Hypoxia has well established physiological effects on many organisms, and in fish has been shown to share a similar molecular pathway as hydrocarbon exposure (via cross-talk of the ARNT/HIF-1β protein). Thus, the possible co-occurrence of these two stressors may have unanticipated effects through synergistic interactions. We are evaluating the combined effects of short term (48 hr) exposures to hypoxia, Corexit 9500 and chemically dispersed Southern Louisiana Crude Surrogate Oil (CEWAF) by following mortality in one day post hatch Sheepshead minnow (*Cyprinodon variegatus*) larvae held under normoxic (ambient air) and hypoxic (5% O2) conditions. Preliminary results with Corexit alone indicate the combined effect of hypoxia enhances toxicity observed in response to either treatment alone. We anticipate the results obtained with CEWAF exposures will be even more striking.

Biodegradation of Total Bioavailable and Speciated Hydrocarbons from Dispersed Oil in Seawater

T. Parkerton[1], R. Prince[2], D. Letinski[2], A. Redman[2]
[1]ExxonMobil Biomedical Sciences Inc, Houston, TX, [2]ExxonMobil Biomedical Sciences Inc, Annandale, NJ

Past research has shown that passive sampling measurements performed using polydimethylsiloxane coated solid phase microextraction (SPME) fibers, followed by subsequent thermal desorption of fibers and GC-FID quantification of absorbed hydrocarbons, can be used to define bioavailable hydrocarbons that determine the acute aquatic toxicity of various dispersed oils. In this study, SPME analysis of physically and chemically dispersed Endicott crude oil water accommodated fractions (WAF) were performed at different times to determine the rates at which bioavailable hydrocarbons biodegrade in seawater. In addition, conventional solvent extraction was also performed followed by GC/MS analysis to quantify specific hydrocarbons and corresponding biodegradation rates after normalization to hopane which served as a conserved marker. Results demonstrated that bioavailable hydrocarbons in the chemically dispersed treatment at test initiation were approximately a factor of five higher than in comparable physically dispersed tests. Furthermore, bioavailable hydrocarbons were shown to biodegrade rapidly in both dispersion treatments with a half-life of 1 to 2 days. These results indicate a rapid decrease in predicted toxicity of dispersed oil as a result of biodegradation, even without taking dilution into account. Half-lives for speciated hydrocarbons showed a wider range across both dispersion treatments, and will be discussed in the context of current quantitative structure-biodegradation relationships.

Sorption of DOSS to Coastal Gulf of Mexico Sediments

B. S. Adewale, B. Brownawell
Stony Brook University, Stony Brook, NY

Surfactant components of oil spill dispersants are particle reactive and sorption to particles affects their bioavailability and fate. Our interest is in the properties of surfactants (structure and concentration) and sediment particles that influence sorption, and the properties of solution (pH and constituents of sea salt) that shed light on controlling mechanisms. Anionic 1,4 bis(2-ethylhexyl) sodium sulfosuccinate (DOSS), a surfactant in Corexit dispersants, has been observed in appreciable concentrations in Gulf of Mexico sediments, illustrating the need to better understand interactions with settling particles. There are similarities in the magnitude of sediment-water distribution coefficients (Kd, which approaches 1000 L/Kg for the highest TOC sediment), as well as the effect of sediment (organic carbon content) and solution properties (pH and salinity) on sorption with that observed in prior studies with similarly hydrophobic linear alkylbenzene sulfonates (LAS). However, there is increasing evidence that there are important differences between DOSS and other anionic surfactants. While divalent Ca and Mg impart greater effects on sorption than Na, the effect of Na is larger than for LAS and greater than can be explained by purely electrostatic interactions. Importantly, we have observed that DOSS can sorb very strongly to glass surfaces (largely above the air-water interface) from seawater solution, a phenomenon not observed in sediment suspension. Large and variable losses of DOSS to container surfaces have been observed by others. Potentially relevant is the large body of research that explores the very unique effects that DOSS has at aqueous-nonaqueous interfaces.

Evaluation of the Cactus Based-Mucilage Dispersant on Its Toxicity and Surface Tension and Droplet Size of Dispersed Crude Oil

F. Guo, D. Stebbins, T. Peng, S. Thomas, R. Toomey, N. Alcantar
University of South Florida, Tampa, FL

The purpose of this research is to evaluate the effect of the cactus plant-based mucilage on the toxicity, surface tension, droplet size and stability of dispersed crude oil in oil/water emulsions. The mucilage is extracted from the cactus plant, and the extraction process yields two types of mucilage: the non-gelling extract (NE) and the gelling extract (GE). A standard EPA toxicity test using Daphnia magna colonies exposed to both NE and GE mucilage extracts in concentrations ranging from 0 to 5000 mg/L has shown that mucilage can be classified as non-toxic to the evaluated species with a LC50 above 2000 mg/L. Cactus mucilage extracts and conventional dispersants has been evaluated by testing the surface tension and measuring the droplet size of oil/water emulsions under different concentrations, including three concentrations of oil (3, 6, 30% v/v) and several dispersant to oil ratios (1:1, 1:3, 1:10). Synthetic seawater and surrogate oil from BP were used. The results of the dispersion obtaned using mucilage extracts were compared with using conventional dispersants, Corexit 9500A. The surface tensions of emulsions with cactus mucilage were almost the same as with Corexit (both around 30 mN/m). The average droplet size was smaller in the systems with cactus mucilage (1.5% of NE has generated 5 µm droplets) when compared with the systems using the Corexit (1.5% of EC9500A has formed 6.2 µm droplets). In addition, baffled flask test will be perfomed to further test the dispersion effectiveness. Cactus mucilage can be an alternative technology to mitigate the damage that oil may cause to the aquatic ecosystem and minimize undesired effects associated with the use of synthetic dispersants in oil spills.

Effects of Corexit 9500 as a Potential Endocrine Disruptor on Sex Determination of the American Alligator

N. A. McNabb[1], L. J. Guillette Jr.[2], S. Kohno[2]
[1]College of Charleston, Charleston, SC, [2]Medical University of South Carolina, Charleston, SC

The American alligator (*Alligator mississippiensis*) exhibits temperature-dependent sex determination (TSD), in which incubation temperatures during thermosensitive period (TSP) in embryonic development determine sex of the embryo. Estrogen signals also play a critical role in TSD. A single exposure to exogenous estrogen during TSP overrides the effects of temperature, and leads to sex reversal and skewed sex ratios by inducing ovarian development at a male-producing temperature. The alligator is potentially an excellent sentinel species to investigate chronic exposure to environmental contaminants including endocrine disrupting contaminants (EDCs), because it is an apex predator that does not migrate far from its estuarine habitat during its long lifetime. During the 2010 Deepwater Horizon oil spill in the Gulf of Mexico, Corexit 9500 was applied to the surface water and at the wellhead to disperse the oil. We found that Corexit 9500 could potentially be an alligator EDC using an in vitro estrogen receptor 1 (ESR1) reporter gene assay. To pursue this, alligator eggs were exposed to Corexit 9500 at 0.25, 2.5 and 25 mg/g egg weight during TSP to investigate the potential endocrine disruption and effects on gonadal development *in ovo*. Early findings indicated that exposure to Corexit *in ovo* at these doses did not affect viability at hatch-out. Further analyses of gonadal development in alligators exposed to Corexit *in ovo* will be reported. We are now investigating this more thoroughly by interrogating specific components of Corexit and fractions generated by our team members.

The Use of Ephyrae of a Scyphozoan Jellyfish, *Aurelia aurita*, in the Ecotoxicological Assessment of MC252 Oil

B. Echols[1,2], A. Smith[2], G. Rand[2]
[1]University of Maryland Baltimore County, Baltimore, MD, [2]Florida International University, North Miami, FL

Ephyrae (free-swimming larvae, produced asexually) of the scyphozoan jellyfish, *Aurelia aurita*, were evaluated in 96-hr acute toxicity tests for lethal response (i.e., cessation of pulsation) to a standard reference toxicant (cadmium chloride), weathered and unweathered MC252 crude oils, a dispersant (Corexit 9500) and oil-dispersant mixtures. Reference tests demonstrate excellent reproducibility with 4% variation of median lethal concentration values (LC50s), ranging from 1309 to 1503 µg CdCl2/L. The average LC50 for the chemically enhanced water accommodated fractions (CEWAF) of MC252 oil (measured as TPAH, 46 PAHS) was 131±65 µg TPAH/L. The total PAH concentrations in all preparations, including all dilutions for all laboratory testing exposure media represent the highest 3.9 percent of the 10,800 total PAH measurements from water samples collected during DWH. The average LC50 for Corexit 9500 alone (measured as the concentration of dioctyl sodium sulfosuccinate or DOSS) was 3175 ±122 µg DOSS/L. These average LC50s far exceed concentrations of DOSS (ranging from 0-650 µg/L) measured in the offshore water samples from the Gulf of Mexico during the Deepwater Horizon accident. Of the 5,600 field measurements of DOSS, only 12 exceeded the USEPA benchmark of 40 µg DOSS/L. These results suggest that *A. aurita* may be a model organism for toxicity testing and a useful testing organism for determining potential effects to marine jellyfish.

Toxicity of Water Accommodated Fractions of Oil and Oil-Dispersant Mixtures to Early-Life Stages of the Blue Crab, *Callinectes sapidus*

B. Echols[1,2], A. Smith[2], P. Gardinali[2], G. Rand[2]
[1]University of Maryland Baltimore County, Baltimore, MD, [2]Florida International University, North Miami, FL

Blue crab (*Callinectes sapidus*) is an economically important species inhabiting the Gulf of Mexico. Hatchery reared zoea were exposed to water-accommodated fractions (WAFs) of unweathered and weathered MC252 oils. In addition, toxicity of the dispersant, Corexit 9500, and dispersant-oil mixtures were evaluated. Acute tests with WAFs of weathered oil resulted in no discernable toxicity, with average survival ranging from 79 to 86%, compared to 95% in controls. Acute tests with unweathered oil resulted in mortality (92.5-100%) at the highest test concentration (133 µg/L of TPAH, based on 46 PAHs and 4809 µg/L of BTEX), which was within the upper concentrations collected in the field. Toxicity increased with the addition of Corexit 9500 to oil, resulting in substantial mortality (67.5 to 100%) in test concentrations where the mean concentration of dispersant, based on measured dioctyl sodium sulfosuccinate or DOSS, was 3253 µg/L. Dispersant only tests (n=3) had variable results, with survival ranging from 0-85% at the highest concentration and median lethal concentration values (LC50s) of 1220 to >2830 µg DOSS/L. DOSS concentrations (1640 to 7400 µg/L) were substantially higher in laboratory prepared mixtures than those measured (0-650 µg/L) in the Gulf of Mexico during DWH. Of the 5600 field measurements, only 12 exceeded the USEPA Aquatic Life Benchmark of 40 µg/L DOSS.

Polymer Grafted Nanoparticle-based Oil Dispersants

D. Kim, K. Liang, R. Krishnamoorti
University of Houston, Houston, TX

Particle-based oil dispersants mainly composed of inorganic nanoparticles such as silica nanoparticles are considered as environmentally friendly oil dispersants due to their biocompatibility and relatively low toxicity. The oil-water interfacial tension is reduced when nanoparticles segregate to the oil-water interface and this segregation is improved by grafting interfacially active polymer brushes. In this study, surfactant-like amphiphilic block copolymers (POEOMA-b-PS) and gradient copolymers (PAM-g-PMMA) were grafted from silica nanoparticles using a living radical atom transfer polymerization (ATRP) method in order to increase their interfacial activity. We have studied the interfacial activity of such hybrid nanoparticles using pendant drop interfacial tension measurements, and their structure using small angle X-ray scattering. Amphiphilic copolymer grafted nanoparticles significantly reduced oil - water interfacial tension compared to the interfacial tension reduction induced by homopolymer grafted nanoparticles or the corresponding free ungrafted copolymer and it is believed that hydrodynamic particle size and copolymer composition are controlling variables to determine the oil dispersion ability of nanoparticles. Moreover, hard and stable oil - water emulsions were formed by applying the block copolymer grafted nanoparticles due to the formation of interparticle network structures, which were observed by cryo - scanning electron microscopy (SEM). These polymer grafted nanoparticles with improved interfacial activity are expected to be effective emulsion forming and stabilizing agents.

Toxic Effects of Crude Oil, Dispersant and Oil-Dispersant on the Marine Microalgae *Ostreococcus tauri* Assessed by a Luminescent Biosensor Approach

F. Joux[1], N. Chédri[1], F. Bouget[1], P. Schatt[1], W. Jeffrey[2], M. Tedetti[3], C. Guigue[3], M. Goutx[3]
[1]Laboratoire d'Océanographie Microbienne, Observatoire Océanologique, Banyuls sur Mer, France, [2]University of West Florida, Pensecola, FL, [3]Aix Marseille Université, Mediterranean Institute of Oceanography, Marseille, France

The Deepwater Horizon oil spill released an estimated 4.9 M barrels of crude oil into the Gulf of Mexico in July 2010. To mitigate the effect of the oil spill, accelerate natural dispersion, and enhance biodegradation, approximately 1.5 million gallons of a chemical dispersant, Corexit 9500, were sprayed onto the surface or applied at the source of leak. As primary producers, phytoplankton play a major role in marine ecosystem functioning and toxicity of crude oil can be attributed mainly to interferences with the photosynthetic apparatus. In contrast, the surfactants present in Corexit 9500 likely act on membranes. Toxic effects of crude oil, dispersant and oil-dispersant were investigated using a microalgae biosensor, Ostreococcus tauri, expressing luminescence proportionally to the gene expression of Cyclin-Dependent Kinase (CDKA), encoding for a protein involved in the cell cycle. Toxicity of water accommodated fraction (WAF) of MC252 was low (EC50>50,000 ppm). Corexit 9500 enhanced WAF (DEWAF, 1:20) increased the toxicity of Macondo (EC50=12,500 ppm). This higher toxicity can be due to increased bioavailable oil fractions such as alkyl compounds with dispersant. Corexit EC9500A alone had a highly inhibitory effect (EC50= 20 ppm) sufficient to explain the toxicity observed in the DEWAF. This high toxicity of Corexit was also confirmed for natural phytoplankton community (EC50= 10 ppm). Corexit 9500 toxicity for *O. tauri* biosensor decreased after two days of exposure to simulated solar radiation. The *O. tauri* CDKA biosensor provides a high-throughput and sensitive method allowing the exploration of the interactive effects of crude oil and dispersant with other environmental factors or pollutants.

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

Using DNA Adducts to Examine Polycyclic Aromatic Hydrocarbon Exposure in Shark and Bony Fish Populations Impacted by the Deepwater Horizon Oil Spill

J. C. Whalen[1], J. Gelsleichter[1], R. D. Grubbs[2]
[1]University of North Florida, Jacksonville, FL, [2]Florida State University Coastal and Marine Laboratory, St. Teresa, FL

The Deepwater Horizon oil spill (DWH) released approximately 5 million barrels of petroleum into the Gulf of Mexico between April and July of 2010. The Gulf is home to hundreds of natural oil seeps, but the DWH created an atypical environment for localized demersal fish species because of the high concentration of oil and its most toxic components, polycyclic aromatic hydrocarbons (PAHs). Exposure to PAHs generally results in increased expression of metabolic enzymes necessary for biotransforming and excreting these compounds. Occasionally, metabolites from this process can bind to DNA, forming adducts and potentially resulting in mutagenic effects. The objective of this study is to investigate if PAH-DNA adduct formation occurred in several abundant and ecologically important Gulf of Mexico sharks (*Squalus cf. mitsukurii*, *Squalus cubensis*, *Centrophorus cf. niaukang*, *Centrophorus cf. granulosus*) and bony fishes (*Lopholatilus chamaeleonticeps*, *Urophycis cirrata*, *Urophycis floridana*). The presence of DNA adducts was determined by immunocytochemical analysis of blood samples collected from 2011 to 2014. Animals were collected using demersal long lines from the Northeast Gulf at varying distances from the origin of the DWH. Adduct formation was compared to reference sites, located off the West Florida Shelf, and positive controls. Samples are currently being analyzed.

Trophic Structure, Feeding Ecology and Bioaccumulation of Hg in GoM Hagfishes

A. Mickle, R. D. Grubbs, J. P. Chanton
Florida State University, Tallahassee, FL

Hagfishes are common in deep waters of the Gulf of Mexico (GoM). Two out of the three species found in the GoM are endemic and yet very little is known about their life histories and ecology despite being known to provide key ecosystem services. Increased commercial interest and lack of regulation, mostly due to a dearth of knowledge about basic life aspects of these species, has caused hagfish populations to decline in various parts of the world. The objective of this study is to get an insight on the hagfishes from the GoM and investigate trophic structure, feeding ecology and bioaccumulation of Hg on the three species found in the region (*Eptatretus springeri*, *Eptatretus minor*, *Myxine mcmillanae*). Trophic structure and feeding ecology of hagfishes from the GoM collected quarterly from 2011-2014, will be examined using δ13C, δ15N and δ34S stable isotope analysis and by examining stomach contents using molecular genetic analysis. Muscle samples will be analyzed for Total Hg (THg) content and Methyl-mercury (MeHg) and Inorganic Hg (IHg) concentrations and compared for potential variations in bioaccumulation levels caused by the changing conditions that originated after the Deepwater Horizon oil spill. Preliminary δ15N and δ34S signatures indicate that these species were feeding on slightly different trophic levels suggesting variation in their feeding strategies. Early Hg analysis shows a positive correlation with δ15Nvalues. However, IHg concentration is relatively high when compared to other benthic deep sea species which could indicate higher sediment ingestion or the potential for hagfish to perform demethylation.

Changes to the Metabolome of the Deep-Sea Coral *Leiopathes glaberrima* as a result of Exposure to Crude Oil and the Chemical Dispersant, Corexit 9500

C. Campbell[1], M. Devlin-Durante[2], **S. Vohsen[2]**, I. Baums[2]
[1]The University of Glasgow, Glasgow, United Kingdom, [2] Pennsylvania State University, University Park, PA

Previous work in our lab showed that oil and dispersant exposure affects the health, survival, and gene expression of deep-sea corals. Here we investigated changes in the metabolome of *Leiopathes glaberrima* and associated microbes in response to oil and dispersant exposure. We conducted a non-targeted, Liquid Chromatography-Mass Spectrometry (LC-MS) metabolomic analysis of *L. glaberrima* exposed to three treatments; oil, dispersant and a mixture of both. Replicates of each treatment and the control (total 120) were run on a Water C18 CSH column for lipids. We found that oil, dispersant and a mixture of both significantly altered metabolomes after 48 and 72 hrs of exposure in relation to the control. In particular, we observed increases of a specific Lysophosphatidylethanolamine and decreases of two Phosphoethanolamines and Phosphocholines in all treatments. Changes in other LPEs and PCs were specific to the oil treatment and the mixture treatment. We also found an increase in two Lyso-Platelet-activating factors (C-16 and C-18:1) in all treatments while one (C-18) increased in both the oil and mixture treatments. Together, these results suggest that the immune response, cell signalling, and cell-membrane functionality of *L. glaberrima* were affected to varying degrees by exposure to oil, dispersant and a mixture of both. Identification of other compounds and further analyses comparing the overall effect on the metabolome between treatments is underway.

Comparative Records of Persistent δ13C Depletion in Benthic Foraminiferal Carbonate following the Deepwater Horizon and Ixtoc events

M. A. Glabach[1], P. T. Schwing[1], E. A. Goddard[1], D. J. Hollander[1], M. L. Machain-Castillo[2], J. A. Sánchez-Cabeza[2], A. Gracia[2], C. Ruiz[2]
[1]University of South Florida, St. Petersburg, FL, [2]Universidad Nacional Autonoma de Mexico, Mexico City, Mexico

Sediment cores were collected in both the Northeastern and Southwestern Gulf of Mexico (GoM) in order to provide comparative analyses of the Deepwater Horizon (DWH, 2010) and Ixtoc (1979) petrochemical releases on benthic foraminiferal (*Cibicidoides spp*.) shell (test) chemistry. The δ13C of foraminiferal carbonate was determined with depth at two stations northeast (35-65 NM) of the DWH site and three stations (110-160 NM) southwest of the Ixtoc site. The sediment cores were dated using short-lived radioisotopes (210Pb) to define pre- and post-spill intervals. Benthic foraminiferal carbonates incorporate the depleted δ13C signal of petrocarbon sources associated with chronic and long-term exposure to natural seeps. This comparative study demonstrates that benthic foraminifera can also preserve the depleted δ13C signal of short-term (months) but spatially widespread petrochemical release from DWH and Ixtoc. Initial results show persistent and enhanced δ13C depletion in benthic forminferal carbonates of up to 0.27‰ at the DWH sites and 0.21‰ at the Ixtoc sites, relative to pre-spill conditions. These depletions occurred in the aftermath of each petrochemical release and are significantly outside natural variability. Some persistent questions that can be addressed through comparative Ixtoc and DWH records are: 1) what spatial (area and depth) and temporal δ13C records of the Ixtoc event are preserved in the sedimentary archive? and 2) can the record of the IXTOC event be used to characterize and predict the response and recovery rate of the DWH event?

Benthic Foraminifera Density and Richness Patterns in the Southern Gulf of Mexico 25 Years after the Ixtoc Oil Spill

M. L. Machain-Castillo, A. Gracia, H. Alexander-Valdés, A. Rodríguez-Ramírez, X. A. Nava-Fernández, L. E. Gómez-lizárraga
UNAM, Ciudad de México, D. F., Mexico

Benthic Foraminifera from surface sediment samples collected in 2004 in the area surrounding the Ixtoc-I, SWGoM were analyzed to evaluate their population characteristics 25 years after the Ixtoc-I oil spill. Organic carbon and hydrocarbon contents were also measured in the sediments for comparison purposes. Organic carbon content in the sediments varies from 0.1 to 1.9% being more abundant offshore Terminos Lagoon and the Grijalva-Usumacinta rivers. Total HAPs content varies from 0.326 - 30.185 µg/kg ± 8.349 in the area (regarded as non-harmful in other areas). Diversity and community structure of Foraminifera has often been used as an indication of community and environment health. Foraminiferal populations in the samples studied are abundant and diverse, despite the low organic carbon contents. The number of species (n= 20 to 37, depending on depth) and mean density of ≥3000 individuals/g of sediment (living + dead faunas) are similar to other areas of the SWGoM outside the oil exploitation areas. Their tests do not exhibit deformities and scanning electron microscopy shows, in general, no structural damage to the foraminiferal shell. Although foraminiferal community has been chronically exposed since 1979 to oil hydrocarbons from the oil industry in the area, their diversity and structure seem to correspond to chemical unpolluted areas. It implies that after 25 years from Ixtoc-I oil spill, benthic foraminiferal communities have recovered.

Monitoring Recovery of Mesophotic Corals: 2011-2014

M. Silva[1], P. Etnoyer[2], I. MACDONALD[1]
[1]Florida State University, Tallahassee, FL, [2]NOAA, Charleston, SC

Injured and uninjured octocorals and antipatharian colonies were marked and photographed in 2011 on the Mesophotic Pinnacle Reefs (~70 m) offshore Mississippi-Alabama after the DWH oil incident. The same corals were visited in 2014 in order to quantify their health status after 3 years. In total, four of ten makers (3 in Alabama Alps Reef and 1 in Roughtongue Reef) were visited and the coral colonies of the area were photographed to stablish and quantify health status. Preliminary results suggest that corals colonies that presented more than 40% of their soft tissue injured in some degree or, as we call, a fatal injury such as tissue necrosis or bare skeleton in a main branch would not be able to improve their health situation. On the other hand, corals that presented less of 40% of injury or/and preliminary sings of stress such as retracted polyps and mucus secretion were able to recover. Although these findings are preliminary and further analysis are required, in some degree they are consistent with similar results reported by (White, Hsing et al. 2012) on cold water corals of the Gulf of Mexico.

White, H. K., P. Y. Hsing, W. Cho, T. M. Shank, E. E. Cordes, A. M. Quattrini, R. K. Nelson, R. Camilli, A. W. J. Demopoulos, C. R. German, J. M. Brooks, H. H. Roberts, W. Shedd, C. M. Reddy and C. R. Fisher (2012). "Impact of the Deepwater Horizon oil spill on a deep-water coral community in the Gulf of Mexico." Proceedings of the National Academy of Sciences of the United States of America 109(50): 20303-20308.

Stained Benthic Foraminifera Patterns from Deep Sea Sediments in the Gulf of Mexico

A. Egremy, J. C. Herguera
CICESE, Ensenada, Mexico

Here we present new results on the benthic foraminifera distribution patterns in sediment samples collected from slopes and the abyssal plain of the Gulf of Mexico (GM) south of 25°N. Our observations show the importance water depth and food availability to explain their abundance patterns. We used several cores extracted from nine stations at depths ranging between 1200 to 3800 m depth collected during the oceanographic cruise XIXIMI-3 aboard the research vessel BO/Justo Sierra during February and March of 2013. From each station we sampled the first 3 cm at 1 cm resolution which were preserved in a 4% formalin sea-water solution to which we added Rose Bengal for the identification of the living or recently alive benthic foraminifera.Our results show a distinct enrichment in their abundances in cores collected from the slopes of the GM, where these abundances range between 5 to 9 stained benthic foraminifera/cm2. In contrast with the abyssal plain region where typical abundances clustered around 2 benthic foraminifera/cm^2. These observations suggest the influence of a higher flux of organic matter to the slope regions than to the abyssal plain sediments. Another pattern emerged in our observations related to the higher abundances of agglutinated foraminifera in the abyssal plain region in contrast with the slopes. This observation agrees with a similar one reported by Bernhard et al. (2008) in spite of the different treatment we carried in our sediment samples. We will explore several explanations for this observation that range from the carbonate saturation state in these deep waters to food availability to try to explain this important distribution pattern.

Effects of the Deepwater Horizon Oil Spill on Alabama Coastal Fish Populations: Observations from a Recreational Fishing Tournament

C. Robison
University of North Florida, Jacksonville, FL

In April 2010, the Deepwater Horizon Oil Spill released almost 5 million barrels of liquid petroleum into the northern Gulf of Mexico, creating risks for the health of resident organisms. A sizable portion of oil moved onshore to the coastal habitats of states including Louisiana, Mississippi, and Alabama. As part of studies to determine whether coastal Gulf animals were affected by the oil spill, researchers were fortunate to obtain biological samples from sharks and bony fishes collected from an annual (July) recreational fishing tournament, the Alabama Deep Sea Fishing Rodeo, from 2012 to 2014. To examine the health of Alabama fish populations, these samples were tested for a series of biomarkers indicative of exposure to polycyclic aromatic hydrocarbons (PAHs), the most toxic components of crude oil. More specifically, levels of several inducible PAH-metabolizing enzymes, including glutathione-S-transferase and cytochrome P4501a1 in the liver, as well as the relative concentration of PAH metabolites in bile were measured. Data suggest that the levels of PAH biomarkers may differ based on species, perhaps indicating variations in level of exposure. Variations in PAH biomarkers associated with time since the occurrence of the oil spill, as well as differences in these data versus those from reference site animals, are discussed.

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

Recovery after the Deepwater Horizon Oil Spill: Shoreline Oiling Effects on Marsh Erosion

S. M. Bourgoin[1], D. R. Deis[2], I. A. Mendelssohn[3], Q. Lin[3], A. Hou[3], J. Fleeger[3]
[1]Atkins, Tallahassee, FL, [2]Atkins, Jacksonville, FL, [3]Louisiana State University, Baton Rouge, LA

The release of a government-estimated 4.9 million barrels of oil from the Deepwater Horizon (DWH) event in 2010 exposed the nation's largest and most productive wetland-estuarine environment to an unprecedented potential for environmental damage. In general, oil spills can cause widespread impacts to the structure, function, resilience and sustainability of coastal wetlands depending upon oil type, volume, degree of weathering, mode of contact and other environmental and biotic factors. Impacts of the oil release on the shoreline salt marshes along northern Barataria Bay, LA were investigated. Our sampling sites span Barataria Bay from Wilkinson Bay to Bay Jimmy and represent areas of marsh shoreline classified as reference (no observed oil impact), moderately-oiled (some oiling observed), and heavily-oiled (significant oiling observed). Available aerial images of the region were obtained over a time series to examine pre-and post-release marsh erosion. The availability of aerial images was inconsistent prior to the release, but consistently available bi-annually after the release. The heavily oiled stations experienced greater average erosion over the time-series period (both pre- and post-release) and within each year compared to reference marshes; however, variability was high among stations.

The Weathering and Distribution of Petroleum Hydrocarbons along Coastal Louisiana following the Deepwater Horizon Oil Spill

E. Overton, S. Miles, B. M. Meyer, L. Hooper-Bui, G. Olson, R. Turner
Louisiana State University, Baton Rouge, LA

Oil is a complex mixture of thousands of hydrocarbons spanning a wide range of molecular sizes and structures. When this mixture is spilled into marine environments, the mixture undergoes a complex transformation known as oil weathering, which changes the spilled oil's capacity for environmental impacts and distribution in near shore coastal waters. Oil released at depth from a well blow out, such as the Deepwater Horizon incident undergoes additional dissolution and dispersion in deep waters before droplets reach the surface and start the conventional weathering and movement processes. Ultimately, most oil is degraded by indigenous petroleum degrading microorganisms to biomass and CO2. We will discuss the hydrocarbon compositional changes in sediment samples collected along the Louisiana coastline during and for four years after the spill, and make the distinction between typical background compositions and weathered Macondo 252oil., with special emphasis focused on the environmental composition of toxic compounds found in petroleum Of the three classes of petroleum hydrocarbons (the saturate normal, branched, and cyclic structures; the aromatic parent and alkyl homolog PAH structures; and the degradation resistant hopane, sterane and triaromatic biomarker compounds) aromatic compounds are of most concern because of their associated toxicity towards marine and terrestrial organisms and their photo enhanced reactivity. In addition to the weathering changes of petroleum hydrocarbons, the composition of hydrocarbons in non-impacted samples in Louisiana coastal marshes will be described.

New Insights in the Exploration of Cryptic Microbiota Associated with Pre- and Post-DWH Oil Spill Rhodoliths Using Next-Generation and Sanger Sequencing: A Case for the NW Gulf of Mexico

T. Sauvage, W. Schmidt, S. Fredericq
University of Louisiana at Lafayette, Lafayette, LA

Prior to the 2010 BP Deepwater Horizon oil spill disaster, rhodolith beds at Ewing Bank in the northwestern Gulf of Mexico (~28o05.710'N, 91o01.289'W) harbored diverse algal assemblages at 55-75m depth. As of September 2014 these beds have not recovered to pre-spill abundance in terms of species richness and abundance. Nonetheless, in laboratory studies, these algal-denuded rhodoliths maintained as live rocks in 20-gallon closed systems at UL Lafayette Lafayette have gradually became covered by a suite of macroalgal (red, green and brown seaweeds) germlings from seemingly ecologically cryptic stages (e.g. spores, filaments) present in the epilithic and/or endolithic microbiota of the rhodoliths nodules. Using universal 16S rDNA (V region) and tufA primers targeting photosynthetic biodiversity (prokaryotic and eukaryotic), we newly establish the phylogenetic profiles of several pre- and post-spill rhodolith microbiota to demonstrate their critical role as refuge and marine seedbanks mediating algal community recovery in face of environmental stochasticity caused by natural or anthropogenic causes such as the Deepwater oil spill.

Comparing Fishing Pressure and Oil Spill Impacts for Northern Gulf of Mexico Near-Coastal Fish Assemblages

J. Schaefer, N. Frazier, J. Barr
University of Southern Mississippi, Hattiesburg, MS

Coastal ecosystems along the northern Gulf of Mexico are highly productive and impacted by fishing and petroleum industries in different, sometimes contrasting, ways. As a result of the April 2010 Deepwater Horizon (DWH) incident, oil and oil dispersants were introduced into the northern Gulf of Mexico. At the same time, large portions of the Gulf of Mexico were closed to commercial and recreational fishing for most of the 2010 summer. This presents a unique opportunity to study potential impacts of two disparate types of anthropogenic disturbance. We compare near-coastal fish assemblage data (396 samples representing over 41,000 individuals and 103 species) from pre-DWH (before 2010) and post-DWH (2011-2013) to assess potential changes in abundance, diversity (alpha, beta and gamma), and assemblage structure. Post-DWH assemblages were characterized by high abundance in 2011 (catch per unit effort across all species was 2.5 times higher than in any other year) that was most pronounced in medium sized species that are direct targets of commercial fishing or likely bycatch. Abundances returned to levels similar to pre-DWH in 2012 and 2013. There were no differences in pre and post-DWH levels of diversity, and shifts in assemblage structure were consistent with increases driven by reduced fishing pressure. While other assemblages and ecosystems may respond differently, our data are consistent with near-coastal fish assemblage effects of DWH being masked by much larger responses to reduced fishing pressure. Rigorous empirical data from other systems are required to assess potential DWH impacts across the range of ecosystems potentially affected.

Deepwater Horizon Oil Spill and Gulf of Mexico Shelf Hypoxia

N. N. Rabalais[1], L. M. Smith[2], R. E. Turner[3], E. B. Overton[3]
[1]Louisiana Universities Marine Consortium, Chauvin, LA, [2]Your Ocean Consulting, LLC, Knoxville, TN, [3]Louisiana State University, Baton Rouge, LA

The northern Gulf of Mexico 'dead zone' received much media attention in 2010, as the distribution of Macondo oil in the surface waters overlapped with typical hypoxic area. A prior study of data from July 2010 in an area from the Mississippi River delta to the Atchafalaya River delta indicated that there was no difference in July 2010 compared to mid-summer data from 1989 to 2010. We have further examined summer 2010 (May to July) dissolved oxygen conditions and ancillary parameters to determine if there was a difference related to the presence of aromatic hydrocarbons from the spill. Data for an 8-station transect offshore of Terrebonne Bay and a 7-station transect offshore of Atchafalaya Bay for May, June and July were compared using multivariate techniques. Although oil was present in the surface and bottom water during the May cruise, the water column was well-mixed and bottom oxygen values remained high. Low oxygen events occurring in June and July were related to increased stratification, decreased wind speed and decreased surface salinity, suggesting that hypoxia was formed from typical forcing factors. Oil sample analyses did not detect significant oil exposure within the hypoxic area in July. To further compare the summer 2010 oxygen dynamics with the full 30-year NGOMEX data set (1984-2014) we used predictive hypoxia modeling and a multivariate analysis. The estimated size of the hypoxic zone in 2010 was 99% of the predicted value, suggesting that the net effect of the 2010 oil spill on the hypoxic zone size was negligible. The multivariate analysis indicated that 2010 was similar to other years with high river discharge, Easterly winds, and the presence of a tropical storm/hurricane (TS Bonnie in July 2010).

The Effects of the DWH Oil Spill on the Distribution of Crab Megalopae, Mussels, and Snails within Terrebonne Bay, LA Four Years after the Spill

E. Robinson[1], N. Rabalais[2]
[1]Louisiana State University, Baton Rouge, LA, [2]Louisiana Universities Marine Consortium, Chauvin, LA

The impacts of the Deepwater Horizon oil spill on the distribution of marsh organisms after the spill are relatively unknown. These data are part of a field study examining the distribution of crab megalopae, mussels (*Geukensia demissa*), and snails (*Littorina irrorata*) in Terrebonne Bay, Louisiana after the DWH Oil Spill. Crab megalopae were collected at six marsh sites over a one-week period in August 2013 and August 2014. Mussels and snails were collected along 10 m transects at four marsh sites in April 2013, October 2013, and October 2014. Sediment samples were collected at each site and tested for aromatic and alkane hydrocarbons. Preliminary analysis suggests that the distribution of these organisms is not affected by the oil spill three to four years later. Other variables such as hydrodynamics, sediment properties, and vegetation cover may have a greater influence on the distribution of these organisms after the spill. Future research will examine the oil's sublethal effect on megalopal crab settlement behavior as well as hydrocarbon accumulation within mussel and snail shells.

Evidence of Cross-Shelf Inorganic Carbon Export in the Northern Gulf of Mexico

H. Wang[1], X. Hu[1], W. Huang[2], W. Cai[2], J. Xue[3]
[1]TAMUCC, Corpus Christi, TX, [2]University of Delaware, Delaware, DE, [3]University of Texas at Austin, Port Aransas, TX

To explore carbon dynamics in the ocean margin influenced by the Mississippi River, we calculated column inventory of dissolved inorganic carbon (DIC), dissolved inorganic nitrogen (DIN) in the upper water column (200 m) of the continental slope (water depth 250 m-750 m) off the northern Gulf of Mexico in January, April, July, October, 2009, and March 2010. DIC inventory (DICinv) increased from January, April, reached a maximum in July, then decreased in the following two seasons. DIN inventory (DINinv) followed the same trend as DICinv. The ratio between DICinv and DINinv change was 5.8, close to the Redfield ratio (6.6), suggesting a biological control on the coupled changes between DICinv and DINinv. We hypothesize that this slope water DIC buildup was due to large lateral transport of near coastal primary production along with respiration signal, both of which were results of excess nutrient runoff from the Mississippi River. This carbon transport coincided with offshore river plume transport affected by upwelling winds, as both physical models and field observations suggest. Further observations following the Deep water Horizon oil spill also confirmed this type of episodic but nonetheless significant carbon export, which may be an important pathway for transporting atmospheric CO2 into the open ocean in the form of DIC, through the coupling between eutrophication-induced primary production and subsequent remineralization.

Uptake and Deposition of Pyrogenic and Petrogenic PAHs on *Spartina* Leaves and Transfer to Marsh Periwinkle Snails (*Littoraria irrorata*)

Y. Mohammed, V. Elango, J. Pardue
Louisiana State University, Baton Rouge, LA

The uptake of PAHs by plants via particle deposition onto plant surfaces, partitioning into waxy cuticles or translocation through the xylem may be an important route of exposure in Gulf Coast salt marshes impacted by the Macondo spill. Objectives of this study are to compare and contrast the relative uptake and deposition of petrogenic and pyrogenic PAHs in Spartina leaves in impacted marshes and whether these compounds are transferred to marsh periwinkle snails who spend a significant portion of their life cycle on *Spartina* leaf surfaces. Two locations were evaluated in this study; a lightly oiled, saline marsh near Port Fourchon, LA and a less saline, heavily oiled marsh near Bay Jimmy in the Barataria Basin, LA. Using previously published methods for sequential extraction of PAHs in plants, PAHs were measured in surface deposited particles (EDTA extraction), within the cuticle (dichloromethane extraction) and within the plant tissues (accelerated solvent extraction). Sampling was conducted in summer and winter in 2013 and 2014. Petrogenic PAHs, primarily alkylated naphthalenes and phenanthrenes, were measured in concentrations ranging from 1-80 ug/g on a plant wet weight basis. Dibenzothiophenes and chrysenes, PAHs present in MC252 with lower Henry's Law constants, were not observed in plant tissues. Compounds were found primarily in the cuticle but PAHs were also detected in surfaces particles and plant tissues. An identical suite of PAHs were measured in marsh periwnkle snail tissue sampled from *Spartina* leaf surfaces at Bay Jimmy. Results demonstrate an important PAH exposure pathway operating years after the spill.

High Site Fidelity of the Gulf Killifish (*Fundulus grandis*) in Northern Gulf of Mexico Marshes: An Empirical and Modeling Approach to Help Address Oil Effects

C. Martin[1], O. Jensen[2], K. Able[3], F. Fodrie[4], P. Lopez-Duarte[3], B. Roberts[5]
[1]Louisiana State University, Baton Rouge, LA, [2]Rutgers University, New Brunswick, NJ, [3]Rutgers University Marine Field Station, Tuckerton, NJ, [4]University of North Carolina, Chapel Hill, NC, [5]Louisiana Universities Marine Consortium (LUMCON), Chauvin, LA

The gulf killifish (*Fundulus grandis*) has been highlighted as a sentinel species for studying impacts of the Macondo oil spill, largely as a result of its high abundance, widespread distribution, intermediate trophic position, and high stress tolerance. However, its home range and dispersal capabilities remain unclear. Given the spatial scale between many oiled and unoiled sites (10s-100s of meters), this information is essential for use of *F. grandis* as a model species. Here, we present the results of a field study to determine the site fidelity of gulf killifish (>40mm TL) using 4 different marsh creeks (<60 m in length) near Cocodrie, LA. Wire tags were injected into the dorsal musculature of ~100-200 fish per site before release at a central point in each creek. Recapture efforts were made at 5-10 meter intervals along each creek (30-90m) 1-2x per month up to 1 year post-release. A dispersal model was fit to the recapture data and used to understand the spatial and temporal scales of dispersal. Results indicate that *F. grandis* exhibit high site fidelity, with initial recapture rates as high as 49% and some recaptures occurring after 1 year. These data suggest that observed responses to oil are likely to be local and *F. grandis* likely provide reliable metrics of site-specific oil exposure throughout the region and are critical to the development of reliable modeling approaches.

Trials and Tribulations of Gulf of Mexico Algae and Macrocrustaceans Inhabiting Deep Banks Offshore Louisiana: What Have We Learned since the 2010 Deepwater Horizon Oil Spill?

O. Camacho, K. Kailee, S. Self-Krayesky, G. Rees, J. L. Richards, T. Sauvage, W. Schmidt, B. Thoma, D. Venera-Ponton, D. L. Felder, S. Fredericq
University of Louisiana at Lafayette, Lafayette, LA

A summary of important insights centers around the observations that seaweeds and macrocrustaceans at ~55-75m depth offshore Sackett and Ewing Banks, hard banks offshore Louisiana in the NW Gulf of Mexico, have not recovered to pre-oil spill levels in the field. What happened to the taxa that were so diversity-rich pre-spill? Are algal populations from other regions of the Gulf of Mexico helping in the re-establishment of populations that inhabited the deep NW banks prior to the oil spill? Has there been a shift in species diversity from pre- to post spill? Can algal spores, unicells, propagules, germlings, survive the effects of an oil spill? These questions will be illustrated based on our new findings in macroalgal (Chlorophyta, Phaeophyceae, Rhodophyta), dinoflagellate, and macrocrustacean biodiversity research.

Spatial Patterns in Soil Biogeochemical Process Rates along a Louisiana Wetland Salinity Gradient in the Barataria Bay Estuarine System

B. J. Roberts[1], M. W. Rich[1], H. L. Sullivan[1], R. Bledsoe[2], M. Dawson[3], B. Donnelly[4], J. M. Marton[1]
[1]Louisiana Universities Marine Consortium (LUMCON), Chauvin, LA, [2]Nicholls State University, Thibodaux, LA, [3]Oberlin College, Oberlin, OH, [4]Villanova University, Villanova, PA

Louisiana has the highest rate of coastal wetland loss in the US. Louisiana wetlands also experience numerous other environmental stressors including changes in salinity regime (increases from salt water intrusion and decreases from creation of river diversions) and climate-related changes in vegetation (e.g. expansion of *Avicennia germinans* into salt marshes). We examined how these changes influence biogeochemical process rates important in regulating carbon balance and the cycling, retention, and removal of nutrients. Specifically, we measured net soil greenhouse gas fluxes and collected cores to quantify greenhouse gas production, denitrification, nitrification, iron reduction, and phosphorus sorption rates from surface (0-5cm) and subsurface (10-15cm) depths for 3 plots in each of 4 sites along the Barataria Bay salinity gradient: a freshwater marsh, a brackish (7 ppt) marsh, a salt marsh (17 ppt), and a A. germinans stand (17 ppt; adjacent to salt marsh). Most biogeochemical processes displayed similar spatial patterns with rates in salt marsh and A. germinans soils being lower than rates in freshwater and/or brackish marsh sites. Rates in surface soils were generally higher than in subsurface soils. These patterns were generally consistent with spatial patterns in soil properties with water and organic matter content and extractable nutrients decreasing with salinity. These spatial patterns suggest that the ability of coastal wetlands to retain and remove nutrients might change significantly in response to future climate changes and that these alterations to biogeochemical cycling capacity need to be considering when designing and managing future restoration projects especially those involving river diversions.

Recovery of Structure, Function, and Sustainability of Coastal Salt Marshes Impacted by the Deepwater Horizon Oil Spill in Northern Barataria Bay

Q. Lin[1], I. A. Mendelssohn[1], S. A. Graham[1], A. Hou[1], J. W. Fleeger[1], D. R. Deis[2]
[1]Louisiana State University, Baton Rouge, LA, [2]Atkins North America, Inc., Jacksonville, FL

Louisiana's Mississippi River Delta, especially coastal shoreline salt marshes, bore the brunt of impact from the Deepwater Horizon (DWH) oil spill. We have conducted a series of field studies for more than 4 years to assess oil impacts to coastal salt marshes and their subsequent recovery of structure, function and sustainability. In salt marshes of northern Barataria Bay, one of the most heavily oiled habitats, we established replicated field stations that received heavy, moderate and no oiling. Surface soil total petroleum hydrocarbon concentrations in the heavily oiled marshes were 511 (±231) mg g-1 9 months after the spill, and decreased to 100 (±52) mg g-1 48 months after the spill. Heavy oiling caused almost complete mortality of marsh plants, impaired subsequent recovery, and changed vegetation structure of shoreline marshes from a *Spartina alterniflora-Juncus roemerianus* community to mostly *Spartina*. In contrast, plants of moderately oiled marshes were able to recover within two years after the spill, though initial impacts were evident, especially for *Juncus*. Species-specific oil impacts resulted in no recovery of *Juncus* in heavily oiled marshes and delayed recovery of *Juncus* in moderately oiled marshes. Detrimental effects of heavy oiling on live above- and below-ground biomass resulted in significantly weaker soil shear strength, lower sedimentation rates, and higher vertical soil surface erosion rates compared to reference marshes, thus potentially affecting the stability of the oiled shorelines. Further study of the long-term recovery and sustainability of the DWH oil spill impacted marshes is underway.

A Modern View of Diversity and Research Needs among Seaside Sparrow Populations along the Gulf of Mexico

S. Woltmann[1], P. C. Stouffer[2], C. M. Bergeon Burns[2], S. S. Taylor[2]
[1]Austin Peay State University, Clarksville, TN, [2]Louisiana State University and AgCenter, Baton Rouge, LA

Although subspecific variation has been noted in the saltmarsh obligate Seaside Sparrow (*Ammodramus maritimus*) since the late 1800s, there has been no modern reassessment of named taxa using population genetic tools. We sampled 9 populations of Seaside Sparrow across ~ 1800 km of the Gulf Coast (Cameron Co., TX to Levy Co., FL) to examine population genetic structure using 14 microsatellite loci. We found a moderate degree of concordance between population genetic data and named subspecies. Three of the four named subspecies align with genetically differentiated groups in our analysis, but two named subspecies in Florida could not be distinguished using genetic data, and both the geographic and genetic boundaries between two other named subspecies in Texas are unclear within our samples. We discuss how a better understanding of the biodiversity along the Gulf Coast allows for a better evaluation of how and where risk from future oil spills and other disasters to these unique populations varies, and highlight research needs for this group of birds.

Estimating Oil Exposure of Red Snapper and Gag Grouper during the DWH Blowout

D. Lindo-Atichati[1], A. C. Vaz[1], M. Karnauskas[2], C. B. Paris[1]
[1]University of Miami, Miami, FL, [2]NOAA SEFSC, Miami, FL

A critical step to investigate the impacts of oil on coastal ecosystems is to understand the interactions between oil and larval fish in the wake of the DWH Oil Spill. Larval fish are the very foundation of marine populations of the Gulf of Mexico, yet there is little understanding of the oil pathways from the Macondo well to the shallow water column that most fishes use as nursery habitat during their early life history. To reveal these interactions between oil and larval fish we coupled the following modeling approaches: 1) an open source biophysical model that is commonly used in the ichthyoplankton community, the Connectivity Modeling System (CMS); 2) an oil application of the CMS that predicted the depth of the DWH deep plume; and 3) expected spawning habitat maps for red snapper and gag grouper. We include in our models higher resolution species-specific ontogenetic vertical migrations and estimate where high concentrations of oil could have overlapped with critical nursery habitat for red snapper and gag grouper larvae. The outcomes of this work on early life history interactions with oil serve to anticipate exposures of specific larval fish to hypothetical GoM oil deep spills that may occur in the future.

Variation in *Spartina alterniflora* Physiology in South Louisiana Saltmarshes

R. E. Blake, J. Olin, R. Turner
Louisiana State University, Baton Rouge, LA

Saltmarshes are important ecosystems, and in south Louisiana they are valued for filtering nutrients, buffering storm wave and surge impacts, and supporting economically important fisheries, but are vulnerable to stressors such as sea level rise, climate change, and oil spills. Therefore, understanding the dynamic processes that influence the dominant foundation plant in these ecosystems, *Spartina*

alterniflora, is critical. We examined the response of *S. alterniflora* to environmental conditions at twelve sites in Barataria Bay and Terrebonne Bay, Louisiana for three years following the Deepwater Horizon oil spill. We found weak relationships between *S. alterniflora* photosynthesis and sediment shear strength, and amount of shoreline oiling (categories based on 2010 NOAA Shoreline Cleanup Assessment Technique maps). Photosynthesis varied less between sites than between seasons at a given site. This seasonal variability in *S. alterniflora* carbon assimilation is highly correlated, as is plant morphology, with seasonal and inter-annual changes in salinity. Salinity in these bays is largely a function of Mississippi River outflow and thus regional climate and weather patterns in the larger watershed. Therefore, salinity and not oil in the sediments appears to be relatively the most important factor driving the dominant plants, *S. alterniflora* in these south Louisiana saltmarshes two - five years after the Deepwater Horizon oil spill.

Distribution of Petrogenic Polycyclic Aromatic Hydrocarbons (PAHs) in Shrimps after the Deepwater Horizon Oil Spill

H. Fernando, H. Ju, R. Kakumanu, B. Kaphalia, G. Ansari
University of Texas Medical Branch at Galveston, Galveston, TX

The aim of this study was to compare the total polycyclic aromatic hydrocarbons (PAHs) in shrimp collected from Gulf Coast (Louisiana, Alabama, and Mississippi) at different times during September 2011-April 2014. Gulf of Mexico oil spill in April 2010 discharged an estimated 4.9 million barrels of crude oil in open Gulf water. Main concerns of the spill are how PAHs present in crude oil affect marine species and ultimately the overall human health. In response to their concerns we analyzed the presence of petrogenic PAHs in shrimp (brown and white), collected from defined areas in these three states at different time points. A total of 313 samples were analyzed which includes 185 from Louisiana, 53 from Alabama and 75 from Mississippi. Extraction of the PAHs was performed using the QUACHERs/dsPE method and the extract analyzed by Gas chromatography-Mass spectrometry. The total PAHs values obtained were statistically analyzed using the SAS system and GLM procedure. Brown shrimp showed statistically significant differences among various collection periods as well as locations while white shrimp only showed statistically significant differences at various time points. Supported by U19ES02067.

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

Experimental Identification of Multiple States with Hysteresis in Loop Current Systems

J. Kuehl[1], V. Sheremet[2]
[1]Baylor University, Waco, TX, [2]Woods Hole Oceanographic Institution, Woods Hole, MA

The existence of multiple steady flow states in nonlinear fluid dynamic systems has been observed in many situations. Probably the most well-known classical fluid dynamic example is the Coanda (Teapot) Effect, in which a slowly tilted teapot will spill. In Oceanography, the discussion of multiple steady states is generally concerned with the density driven (thermohaline) overturning circulation, which connects the upper and lower ocean and its climatological implications. However, in this work multiple steady

states are identified as the result of a different fundamental balance than the two examples given above. In the context of a gap-leaping boundary current (Loop Current) it is shown that the competition between inertia and vorticity constraints can lead to multiple steady states (gap-leaping or gap-penetrating) with hysteresis. Barotropic and baroclinic rotating table experiments will be presented and various properties of the system will be explored. It is shown that both barotropic and two-layer baroclinic Loop Current systems display multiple steady states with hysteresis. Transitions between gap-leaping and gap-penetrating states are found to be associated with eddy-shedding events, and a transition condition is proposed based on fundamental principles. In addition, a true periodic eddy-shedding Loop Current state is identified and explained through the balance between vorticity advection and vorticity dissipation. As the Loop Current dominates the upper 1000m water column dynamics in the Gulf of Mexico, these findings will significantly inform fate and transport prediction.

Kuehl, J. and V. A. Sheremet, (2014). Two-Layer Gap-Leaping Oceanic Boundary Currents: Experimental Investigation. JFM 740.

Convective Plumes in Rotating Systems

B. Deremble, W. Dewar
Florida State University, Tallahassee, FL

To understand how the DWH oil spill is affected by the rotation of the Earth, we look for the steady states of an axisymmetric model in the rotating and non-rotating cases. This approach allows us to isolate several regimes of convection depending on the strength of the viscous and diffusion coefficients (used here as a parameterization of turbulence). In the non-rotating limit, the linear regime corresponds to a single convective cell pattern dominated by viscous effects. The non-linear regime is characterized by an overshoot above the intrusion level. The inclusion of rotation however strongly affects these classical convection patterns. A new branch of solution emerges at high Reynolds number due to centrifugal effects. We also find regions of the parameter space where multiple steady states coexist, giving rise to a hysteresis behavior.

A Mechanism for Generating Submesoscale Internal Wave Fronts through Interactions with Near-Inertial Waves

Z. Jing, P. Chang, R. Montuoro, J. Kurian
Texas A&M University, College Station, TX

Using idealized hurricane-forced high-resolution (~1 km) Regional Ocean Modelling System (ROMS) simulations and analytical approach, we identified a mechanism for generating submesoscale internal wave fronts (SIWFs) through interactions with near-inertial waves (NIWs). The generated SIWFs have a horizontal spatial scale of 5~10 km and a vigorous vertical velocity of the order of 1 cm/s, propagating along the same direction as NIWs. We show that the SIWFs arise from wave-wave interactions with the large-scale background NIWs as the latter propagate away from the hurricane track. They form in downwelling region of NIWs where the energy transfer from NIWs, the convergence of perturbation energy flux, and the conversion of the potential energy stored in the background stratification work in concert to produce rapid growth of the SIWFs. The SIWFs decay as they enter upwelling region of NIWs. We further examined this mechanism in a realistic simulation of hurricane Katrina in the Gulf of Mexico

and found evidence of similar SIWFs that are consistent with those in the idealized simulations. Implications of these SIWFs for oil spill modeling will be discussed.

Age and Residence Time of Terrestrial Source Water in the Western Atlantic Ocean and Gulf of Mexico

A. C. Todd, R. He
NC State University, Raleigh, NC

Coastal river mouths and bays are the junctions where terrestrial-source water meets and mixes with the open ocean. Once riverine water reaches the coastal ocean, its eventual fate is largely unknown and difficult to trace. Rivers provide fluxes of nutrients and organic matter to the shelf seas, so understanding the eventual fate of this water is important for a variety of biogeochemical processes that occur on the shelf. The fate of terrestrial source water may be described in terms of its age (the time since it reached the ocean) and its residence time (the time it remains on the continental shelf). We implement the constituent-oriented age and residence time (CART) theory within a high-resolution model encompassing the western Atlantic Ocean and Gulf of Mexico to estimate the age of terrestrial source water and its residence time on the region's continental shelves. For this application, 196 river mouths are used as sources of terrestrial water and particular focus is given to water originating from the Mississippi and Atchafalaya rivers. We investigate the spatial and seasonal variability of the water's mean age and compute the residence time within the Gulf of Mexico. From the estimates of age and residence time, we describe the impact of the circulation on the eventual fate of terrestrial waters and provide conjecture on how varying transport time scales may affect the general biogeochemical processes in the coastal ocean.

Parametrization of Surface Particle Transport at Submesoscales in the Gulf of Mexico

A. C. Haza[1], T. M. Özgökmen[1], A. Griffa[2], P. Hogan[3], G. Jacobs[3], E. Coelho[4], A. Poje[5], L. Zamudio[6], E. Ryan[1], D. Bogucki[7], H. Huntley[8], B. Lipphardt[8], M. J. Olascoaga[1], B. J. Francisco[1], A. J. Mariano[1], A. D. Kirwan[8]
[1]RSMAS / University of Miami, Miami, FL, [2]ISMAR-CNR, La Spezia, Italy, [3]NRL, Stennis Space Center, MS, [4]University of New Orleans, New Orleans, LA, [5]City University of New York, New York, NY, [6]Florida State University, Talahassee, FL, [7]Texas A&M University, Corpus Christi, TX, [8]University of Delaware, Newark, DE

A recent Lagrangian parameterization is implemented on a 1/25 degree HYCOM simulation of the Gulf of Mexico circulation in order to correct surface transport at the submesoscales. It combines mesoscale transport from the deterministic Lagrangian Coherent Structures (LCS) and statistical Lagrangian subgridscale (LSGS) models over the submesoscale range. The adaptation of the LSGS model focuses mostly on the relative dispersion metrics. The dispersion statistics of the Grand Lagrangian Deployment (GLAD) drifter data set, and a very high resolution submesoscale permitting HYCOM 1/100 degree simulation are used as references to evaluate the performance of the Lagrangian stochastic model.

GoMRI Mooring Comparison

J. Kuehl[1], N. Wienders[2], S. DiMarco[3], K. Speer[2], P. Hamilton[4]
[1]Baylor University, Waco, TX, [2]Florida State University, Tallahassee, FL, [3]Geochemical and Environmental Research Group, Texas A&M University, College Station, TX, [4]Science Applications International Corporation, Raleigh, NC

Two significant mooring efforts were conducted as part of the GRI I funded research program, led by the GISR and DEEP-C consortia. The GISR array consisted of six moorings located in the vicinity of the Deepwater Horizon spill site (M1 28.5N 88.5W, M2 28.75N 88.75W, M3 28.75N 88.25W, M4 28.5N 89.0W, M5 28.25N 88.75W, M6 28.0N 89.0W). Each mooring consisted of at least 3 recording current meters (RCM 11, hourly) starting 15 meters off the bottom spaced 200 meters apart, an upward looking ADCP (75 KHz, half hourly) and a variety of T-S loggers. The moorings were deployed in July of 2012, turned around in July of 2013 and recovered in late June of 2014. The DEEP-C array also consisted of six moorings located at the head of the De Soto Canyon (M1 29.95N 87.20W, M2 29.90N 87.19W, M3 29.92N 87.13W, M4 29.90N 87.14W, M5 29.82N 87.07W, M6 29.40N 86.98W), some of them shallow (~50 meters), the deepest being at approximately 700 meters. Moorings were equipped with T-S loggers, recording current meters and ADCPs (75 and 300 KHz). The moorings were deployed in May 2012, recovered in May 2013. A statistical characterization of the mooring data will be provided with focus on bottom, intermediate and surface velocity measurements to compare and contrast the local dynamical processes of the two study regions. In addition, pressure data will be presented to identify larger-scale coherent signals between the arrays. The discussion will be cast in terms of SSH forcing and wavelet analysis will be the preferred spectral investigative technique

The SailBuoy Remotely-Controlled Unmanned Vessel: Measurements of Near Surface Temperature, Salinity and Oxygen Concentration in the Northern Gulf of Mexico

L. Hole[1], M. Hasan Ghani[1], I. Fer[2], V. Kourafalou[3], N. Wienders[4], H. Kang[3], K. Drushka[5], D. Peddie[6]
[1]Norwegian Meteorological Institute, Bergen, Norway, [2]Geophysical Institute, University of Bergen, Bergen, Norway, [3]University of Miami/RSMAS Miami, Miami, FL, [4]Florida State University, Earth, Ocean and Atmospheric Science, Tallahassee, FL, [5]Applied Physics Laboratory, University of Washington, Seattle, WA, [6]Christian Michelsen Research, Bergen, Norway

An experimental deployment of a new type of unmanned vessel is presented. The Christian Michelsen Research SailBuoy, a remotely-controlled surface vehicle, sampled near-surface properties during a two-month mission in the northern Gulf of Mexico in March - May, 2013. Averaged over the entire deployment, the vessel speed over ground was 42 ± 30 cm s-1 (± one standard deviation) with a maximum of 180 cm s-1. During the 62 days of the mission, the SailBuoy covered a total range of approximately 400 km in both meridional and zonal directions, with a cumulative total distance of approximately 2400 km. Three parameters were recorded: sea surface temperature, conductivity, and dissolved oxygen. Observed surface temperature and salinity records are compared with remote sensing data and the salinity fields from a regional ocean modeling system, respectively. The absolute difference between remote sensing data to surface temperature is on average approximately 0.5°C. The comparison with the full Gulf of Mexico and the nested Northern Gulf of Mexico HYCOM models demonstrates the validity and usefulness of SailBuoy measurements and the instrument's utility in evaluating fields produced by ocean models having different attributes. The potential of the SailBuoy for

mapping a large-scale river plume, which would be challenging or costly with conventional ship surveys and/or remote sensing, is demonstrated.

Sensitivity of Deep Tracer Release Simulation to Model Resolutions, Advection Schemes and Physics Parameterizations

J. Kurian[1], H. Luo[2], A. Bracco[2], P. Chang[1]
[1]Dept. of Oceanography, Texas A&M, College Station, TX, [2]EAS - Georgia Tech, Atlanta, GA

A suite of dye release simulations is performed using the Regional Ocean Modeling System (ROMS) with differ vertical (60 to 150 levels) and horizontal (7 km down to 1.6 km) resolution, tracer advection schemes, horizontal mixing schemes and vertical mixing closures (M-Y and KPP), as well as horizontal diffusion schemes (biharmonic along S-surfaces and Laplacian along constant z surfaces). Initial and boundary conditions (from HYCOM hindcasts) and atmospheric forcing fields (ECMWF ERA-40 6-hourly fields) are common to all integrations. The dye is released at the Deepwater Horizon (DWH) site on July 28, 2012, 10 days after initializing the model with (common) hindcasted temperature, salinity and velocity fields. The dispersion and trajectory of the dye are then followed for 6 months. Simulations are compared to observations obtained following the DWH spill and data from the GISR release experiment led by Jim Ledwell. Plumes characteristics differ dramatically between simulations. We show that the model horizontal resolution and the choice of the tracer advection scheme are key to the realistic representation of the lateral and vertical extension of the deep plume formed by the dye. A high horizontal resolution is essential to properly simulating the vertical spreading of the plume and its effective (vertical) diffusivity. The best agreement with observations is found whenever submesoscale (1-10km scale) processes are properly resolved. An overestimation up to 50-60% of the plume vertical extension is obtained when using models with horizontal resolution of 5 km. We discuss implications for transport modeling efforts for decision support.

Hydrostatic Modeling of Buoyant Plumes

A. Stroman, W. Dewar, N. Wienders, B. Deremble
Florida State University, Tallahassee, FL

The Deepwater Horizon oil spill in the Gulf of Mexico has led to increased interest in understanding point source convection dynamics. Most of the existing oil plume models use a Lagrangian based approach, which computes integral measures such as plume centerline trajectory and plume radius. However, this approach doesn't account for feedbacks of the buoyant plume on the ambient environment. Instead, we employ an Eulerian based approach to acquire a better understanding of the dynamics of buoyant plumes. We have performed a series of hydrostatic modeling simulations using the MITgcm. Our results show that there is a dynamical response caused by the presence of the buoyant plume, in that there is a modification of the background flow. We find that the buoyant plume becomes baroclinically unstable and sheds vortices at the neutral buoyancy layer. We also explore different scenarios to determine the effect of the buoyancy source and the temperature stratification on the evolution of buoyant plumes.

Observed Surface Current Patterns Influenced by Bathymetry and Wind Forcing along the Shelf of the Northeastern Gulf of Mexico

M. Gough[1], A. Reniers[2], J. MacMahan[3], S. Howden[4]
[1]RSMAS - Univ. of Miami, Millbrae, CA, [2]Delft University, Delft, Netherlands, [3]Naval Postgraduate School, Monterey, CA, [4]University of Southern Mississippi, Hattiesburg, MS

Mean surface currents obtained with HF radar in June 2010 and July 2011 along the shelf of the Northeastern Gulf of Mexico are found to be related to bathymetry and wind-driven Ekman dynamics. Winds from the southeast enhance existing surface flow towards the northeast that follows the 100m isobath, which demarks the edge of the continental shelf. The flow is then directed across isobaths and onshore at the shelf extension of the DeSoto Canyon. This wind and flow pattern was observed in June 2010 when oil from the Deepwater Horizon accident was transported across the shelf and onto the beaches in the vicinity north of the DeSoto Canyon extension. Interestingly, when winds are from the southwest as measured in July 2012, there is a marked increase in surface flow towards the east that is just west of the DeSoto Canyon extension. This flow does not follow the bathymetry and does not support onshore transport. In both June 2010 and July 2012, regardless of wind forcing, mean surface currents over the broad continental shelf near the Mississippi Bight tend to be small (0-10 cm/s). In this region, despite small mean flow, diurnal oscillations of the surface flow can be comparatively large, 30-40 cm/s, where the diurnal variance represents 80% of the total variance. The diurnal oscillations are hypothesized to be a resonance of diurnal wind and tidal forcing coincident with the local Coriolis frequency.

One- and Two-Dimensional Dispersion Quantification from Drifter Triads

H. S. Huntley[1], B. L. Lipphardt, Jr.[1], A. D. Kirwan, Jr.[1], A. Poje[2]
[1]University of Delaware, Newark, DE, [2]City University of New York, Staten Island, New York, NY

The Grand Lagrangian Deployment (GLAD) of 2012 employed a unique launch strategy in the Gulf of Mexico, leading to an unusual, large number of drifter triads. These can be used as nearly collocated repeat samples of 1D two-particle dispersion, providing an estimate of the directional bias inherent in a single-sample strategy. The triads can also be used to derive estimates of 2D dispersion characteristics, in particular area changes and shape deformations, which also directly affect the evolution of the surface signature of an oil spill. Here we report on these statistics and assess their sensitivity to the initial spatial separation scales. Growth rates are found to significantly depend on the sampled flow regimes and hence geography. In the mean, the 2D statistics are more robust to perturbations in initial separation, location, and timing than the 1D statistics; however, they exhibit a larger variance around that mean. A consequence of these findings is that drifters used to observe flow regimes in an area of interest, e.g. the vicinity of an oil spill, should be launched in groups rather than as individuals or even pairs, in order to properly sample the dispersion.

Variability of Cross-Slope Near-Bottom Flow in the De Soto Canyon Region

T. Nguyen, E. Chassignet, D. Dukhovskoy, **S. L. Morey**
Florida State University, Tallahassee, FL

Cross-slope near-bottom flow, or upwelling and downwelling, is an important process for redistributing seawater properties, biota and pollutants between the deep ocean and shallow shelf regions. In this

work, the variability and causes of cross-slope flow and associated vertical motions in the De Soto Canyon region are studied using a multi-decadal HYbrid Coordinate Ocean Model (HYCOM) simulation of the Gulf of Mexico. The density-following trait of HYCOM's hybrid vertical coordinate below the mixed layer is exploited to create time series of cross-slope movement of deep isopycnal interfaces. These and other model-derived time series are analyzed to characterize the cross-slope flow induced by wind-driven motions and mesoscale circulation. In addition to direct impacts of local mesoscale eddies and occasional penetration of the Loop Current into the domain, a mechanism is identified by which Loop Current impact on the southern west Florida shelf can remotely influence the near-bottom cross-slope transport.

Near-Inertial Variability in the Northern Gulf of Mexico

E. V. Maksimova[1,2], R. H. Weisberg[1], D. S. Dukhovskoy[2]
[1]University of South Florida, St. Petersburg, FL, [2]Florida State University, Tallahassee, FL

The oscillations and waves with near-inertial frequency, commonly referred to as near-inertial oscillations (NIO), are thought to be important for mixing both shallow and deep ocean because of their tendency to have large vertical shear and to be quite energetic. Thus, the study of the generation and propagation mechanisms of NIO is needed for proper parameterization of their effects in large-scale models, as well as for the better understanding of their role in particle (such as oil droplets, nutrients, etc.) dispersion. The poster will discuss the characteristics of the NIO in the Northern Gulf of Mexico based on the newest available datasets with the emphasis on the potential of the NIO for mixing in the region.

Quantification of Stokes Drift as a Mechanism for Surface Oil Advection in the DWH Oil Spill

M. Clark, M. Bourassa
Florida State University, Tallahassee, FL

Stokes drift has previously been qualitatively shown to be a factor in ocean surface particle transport, with most studies focused exclusively in near-shore regions. However, Stokes drift has never been comprehensively quantified over a large area and time. Here, Stokes drift is calculated directly from Wavewatch III model data in the Gulf of Mexico for April-July 2010. Its magnitudes are compared between deep and shallow water areas, and against the magnitudes of surface currents and parameterized wind drift. These comparisons are also made specifically for the time period surrounding the passage of Hurricane Alex through the southwestern Gulf of Mexico. While there is not a major difference between the absolute magnitudes of Stokes drift in shallow vs. deep water areas or when compared to wind drift, Stokes drift is larger in shallow water areas relative to surface currents than in deep water. During Hurricane Alex, Stokes drift magnitudes were much larger in the immediate area of the storm, while in the oil spill area there was little change until after the storm was out of the Gulf, at which time swell had propagated into the region, increasing Stokes drift magnitudes.

Beach and Shore-Face Changes along the Galveston Barrier Island after Hurricane Ike: Geomorphologic Features and Their Potential for Oil Spill Monitoring

J. Moya[1], T. Dellapenna[2], C. Weber[1]
[1]Freese and Nichols, Inc., Austin, TX, [2]Texas A&M University, Galveston Campus, Galveston, TX

For years the definition of geologic and engineering concept of the Gulf "Depth of Closure" (DOC) for Galveston Island (GI) was very limited due to the lack of data. In 2006 and 2011, the Coastal Geosciences Group (CGC) at Texas A&M University, Galveston campus (TAMUG) and other partners collected a series of topographic and bathymetric profiles and geological and geophysical sampling and imaging of the dry and wet beach profiles spaced every 3.2 km along the beach and extending 2 km offshore Galveston Island. Hurricane Ike (9/13/2008) was the only major storm to have impacted the beaches during this time frame. Since the GI DOC is now well known, the geomorphologic features identified in these surveys can help in the monitoring of future oil spills by connecting these morphologies to benthic organisms living on these features. Erosional and depositional features characterize the Gulf slope as the natural profiles react to storms. Specific sedimentary structures are dynamic and can be used as indicators of sand movement offshore and oil dispersion on the Gulf bottom. On land, geomorphologic changes can indicate the potential oil dispersion process on the beach and dunes. Combining the results of the topographic, geologic and geophysical data, the approximate volume of sand lost from the shore-face is estimated to be between 2-3 x 106 m3 of sediment. This presentation shows how these shoreface morphologic processes can support future oil spill monitoring programs.

Glider Salinity Correction for Unpumped Conductivity and Temperature Sensors across a Sharp Thermocline

Y. Liu, R. H. Weisberg, C. Lembke
University of South Florida, St. Petersburg, FL

The Gulf of Mexico coastal waters tend to be stratified in spring and summer due to the intense surface heating and reduced wind forcing. Interactions between the Loop Current eddies and the shelf slope could induce strong upwelling and ventilate the continental shelf with cold waters of deep ocean origin that also generate a strong thermocline on the shelf. So, underwater glider observations with unpumped conductivity and temperature sensors often have large errors in salinity data at the depths of thermoclines. We examine different salinity correction methods based on the CTD data collected by the glider on the West Florida Shelf. Salinity corrections are tested using constant and variable thermal lag correction parameters that are determined from the upcast-downcast pairs of glider yoyo profiles. Both methods successfully correct the thermal lag effects of a weak thermocline where temperature change is less than 0.7ºC in 3 m of the water column, but fail to calibrate the salinity spikes near a sharp thermocline where temperature change is ~2ºC within 3 m of the water column. These salinity spikes can be effectively removed by applying a one-dimensional median filter to the data sequence of a glider yoyo in conjunction with the thermal lag correction methods. Thus, a practical approach of glider salinity error correction is proposed, especially for waters of strong stratification and sharp thermocline.

The Coupled Estuarine-Shelf Response of a River-Dominated System during the Transition from Low to High Discharge

B. Dzwonkowski[1], K. Park[2], R. Collini[1], S. Howden[3]
[1]University of South Alabama, Dauphin Island, AL, [2]Texas A&M University at Galveston, Galveston, TX, [3]University of Southern Mississippi, Stennis Space Center, MS

Changes in discharge levels, whether natural or made-man, directly impact estuarine-shelf exchange and will have a critical impact on the transport of oil and oil-derived material. Opportunistic observations captured the coupled estuarine-shelf interactions as the Alabama coastal region transitioned from a period of low to flood river discharge conditions. The period of focus was February 18 to April 10, 2011 during which time a combination of in-situ (water level, salinity and velocity) and remote sensing (ocean color) data provided information on the estuarine and shelf environment prior to, during, and post a major river discharge event that captured a relatively rare spatially synoptic view of the structural evolution of a discharge plume in response to changing forcing conditions. The discharge event generated major changes in the hydrographic conditions and forcing responses within the estuary and on the shelf. The resulting surface advected plume was observed for approximately two weeks, during which time the observed differences in shelf circulation were directly linked to the discharge plume and a plume bulge with anticyclonic circulation was identified at times throughout the event. The plume was exposed to a range of wind conditions which modulated the surface structure: downwelling winds elongated the plume structure and upwelling winds reversed and widened the plume. The influence of wind forcing, even during very low wind (<3.75 m s^{-1}) and large outflow (~7,000 m^3 s^{-1}) conditions, was apparent, as a result of the shallow and wide characteristics of the plume. Anticyclonic bulge regions have only been identified in a few systems and the occurrence of this feature on the Alabama shelf has significant implications on transport and fate of material in this region.

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

Predicting the State and Properties of Deepwater Horizon Oil under Pressure Using the Peng-Robinson Equation of State

J. Gros[1], R. K. Nelson[2], C. M. Reddy[2], S. A. Socolofsky[3], J. S. Arey[1]
[1]EPFL, Lausanne, Switzerland, [2]WHOI, Woods Hole, MA, [3]TAMU, College Station, TX

Being able to estimate the partitioning behavior of the live oil mixture between a gas and a hydrocarbon liquid phase is crucial for valid modeling of the behavior of the emitted fluid. Equations of state are a well-known way to estimate the phase partitioning and phase properties of real fluids under varying pressure and temperature conditions. We used the Peng-Robinson equation of state in combination with the Lin-Duan volume translation to predict the phase partitioning and phase densities of the emitted fluid at pressures and temperatures corresponding to Gulf of Mexico water column depths ranging from 0 to 1500 m. We modeled the emitted fluid based on the 148 compounds quantified on an individual basis by Reddy et al. (2012), together with 131 pseudo-components derived from comprehensive two-dimensional gas chromatography with a flame ionization detector and simulated distillation data for the thousands of compounds not measured on an individual basis. Several correlation methods were used to estimate the required properties, when data were unavailable. The predicted density of the dead oil at surface conditions matches the measured density within <1%. Our

calculations predict a partitioning of the emitted mixture at 1500 m depth of ~30% gas and ~70% liquid hydrocarbons.

Partitioning Behavior of Low Molecular Weight Water Xenobiotic Components throughout the Water Column from Wellhead to Surface

R. Snowdon, **A. Jaggi**, J. R. Radović, S. R. Larter, T. B. P. Oldenburg
University of Calgary, Calgary, AB, Canada

Xenobiotic compounds, such as aromatic hydrocarbons and phenols, are found in petroleum, a naturally occurring complex mixture of hydrocarbons and other species. These distribute into the environment following petroleum spillage, but their partitioning behavior varies with pressure, temperature and the composition of the oil and water. The unprecedented quantity of oil released during the blowout of the Macondo well, which caused the 2010 Deepwater Horizon oil spill, led to an increased interest in the environmental fate of crude oil xenobiotics. A unique, customized oil-water partitioning device was developed to allow us to experimentally determine the partitioning behavior of water soluble oil components from live oils (methane-charged) with saline waters over a range of excess pressure (0 - 17 MPa) and temperature (4 - 80°C). GC-MS was used to elucidate the partitioning of the xenobiotics, including BTEX and C0-C3 alkylated phenols, from petroleum into the water phase, as well as the partitioning trends along varying depths in the water column. This data will aid in near-field and far-field distribution modeling of the environmental fate of crude oil components of interest and assist in the prediction of component migration pathways from potential oil spills. In addition, using a high resolution FTICR-MS, an overview of more complex polar crude oil constituents that partition into water under atmospheric pressure conditions will be presented.

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

Multi-functional Cyclodextrin-Based Systems for the Environmental Remediation of Oil Spills

M. Levine, N. Serio
University of Rhode Island, Kingston, RI

We have developed multi-functional cyclodextrin-based systems for the environmental remediation of toxic oil spills. These systems have three main functions: (a) extraction of aromatic toxicants and toxicant metabolites; (b) detection of the toxicants via proximity-induced fluorescence energy transfer; and (c) detoxification of the aromatic planar toxicants via their conversion to non-planar products. In each of these steps, cyclodextrin plays a crucial role: it binds aromatic toxicants and removes them from the oil into the aqueous phase; it binds the toxicants and fluorophores simultaneously to promote proximity-induced energy transfer; and it catalyzes Diels-Alder cycloaddition reactions to convert the aromatic toxicants to less toxic, non-planar products. We will discuss our research progress in each of these three areas, as well as ongoing efforts to incorporate cyclodextrins in dispersant systems to facilitate the practical application of these systems in oil spill settings.

Simulations-based Design of a Biocompatible Oil Dispersant Additive

S. Benner[1], C. Hall[1], V. John[2]
[1]NC State University, Raleigh, NC, [2]Tulane University, New Orleans, LA

Hydrophobically-modified chitosan (HMC) has been shown to form a gel in the presence of hydrophobic microparticles or vesicles. We are using molecular simulations to design HMCs that promote the formation of a stable oil gel for applications in in-situ oil burning. The HMCs have a comb copolymer architecture with a hydrophilic chitosan backbone and hydrophobic alkane modification chains for the "teeth" of the comb. Coarse grained models of chitosan, HMC, and alkanes have been developed based on atomistic simulations (performed in AMBER) of each species in explicit water. Interaction potentials between each species were derived via Boltzmann inversion of the atomistic radial distribution functions (RDFs). Discontinuous molecular dynamics (DMD) simulations of coarse-grained chitosan in implicit water result in a chitosan persistence length that agrees with experiments. DMD simulations of coarse-grained alkanes in implicit water match all-atom simulations in terms of alkane radius of gyration and end-to-end distance as a function of alkane length. Coarse-grained DMD simulations also allow us to determine how the HMC architecture affects its ability to form a gel with and without oil present in the system. The length of the chitosan backbone (100 - 600 monomers), the length of the modification chains (12 to 24 carbons), and the modification density (2 - 10%) are being varied to determine their role in gel formation. Various degrees of chitosan acetylation (0 - 50%) and charge are also being tested to evaluate their effect on gel formation. Preliminary results show that longer modification chains, higher modification density, and more positively charged glucosamine monomers lead to more significant chitosan network formation.

Halloysite Clay Nanotubes as Interfacially-active Vehicles for Surfactant Delivery in Oil Spill Remediation

O. G. Owoseni[1], E. Nyankson[2], S. Adams[1], A. Bose[3], R. Gupta[2], V. John[1]
[1]Tulane University, New Orleans, LA, [2]Auburn University, Auburn, AL, [3]University of Rhode Island, Kingston, RI

This work indicates a novel concept of integrating particle stabilization of emulsions together with the release of chemical surfactants from the particles for the development of an alternative, cheaper and environmentally-benign technology for oil spill remediation. The application of dispersants to marine oil spills can reduce shoreline impact, lessen the impact on marine organisms and promote oil biodegradation. There are concerns over the potential impacts of existing dispersants on the ecosystem especially the volume of hydrocarbon solvents introduced into the marine ecosystem. Here, we show that naturally occurring halloysite clay nanotubes (HNT) are effective in stabilizing oil-in-water emulsions and can serve as interfacially-active vehicles for delivering oil spill treating agents to the oil-water interface. The HNT assembles in a side-on orientation and form networks at the oil-water interface. The HNTs were loaded with the surfactants, dioctyl sulfosuccinate sodium salt (DOSS), polyoxyethylene (20) sorbitan monooleate (Tween 80) and sorbitan monooleate (Span 80). The HNT was then utilized as an interfacially-active vehicle for the delivery of surfactant cargo. The adsorption of surfactant molecules at the interface serves to lower the interfacial tension while the adsorption of particles provides a steric barrier to drop coalescence. Pendant drop tensiometry was used to characterize the dynamic reduction in interfacial tension resulting from the release of DOSS from halloysite nanotubes. At appropriate surfactant compositions and loadings in HNT, the crude oil-saline water interfacial tension is effectively lowered to levels appropriate for the dispersion of oil spills.

Synthesis of Stearoyl Lactylate Coated Iron Oxide Nanoparticles with Self-Assembled Bilayers for Use in the Formation of Solid-Stabilized Emulsions

P. S. Vengsarkar, C. B. Roberts
Auburn University, Auburn, AL

Iron oxide nanoparticles have highly tunable physicochemical properties which are extremely important in applications like catalysis, biomedicine, environmental remediation and data storage. Specifically, iron oxide based emulsions have been considered as alternative dispersants for oil-spill applications. The objective of this work is to investigate the effect of the primary particle characteristics and stabilizing agent chemistry on the stability of oil-in-water Pickering emulsions. Sodium stearoyl lactylate (SSL) is a FDA approved food additive which was used to coat the iron oxide nanoparticles. SSL is useful in the generation of fat-in-water emulsions due to its high hydrophilic-lipophilic balance and its bilayer forming capacity. Generation of a monolayer or a bilayer coating on the nanoparticles was controlled through systematic changes in reagent amounts. Using a control test-system of n-dodecane (organic phase) and aqueous phases of various pH values, the capacity of these bilayer coated nanoparticles to stabilize oil-in-water emulsions was also systematically determined. The stability of these emulsions with respect to creaming and particle precipitation was studied using various characterization methods. From this study we were successfully able to synthesize iron oxide nanoparticles coated with a novel surfactant (SSL) and were able to generate stable Pickering emulsions which were pH-responsive and resistant to significant destabilization in a saline environment.

Molecular Dynamics Simulations of Hydrophobins Encapsulating Oil and Gas

Y. Chen[1], T. P. Liyana-Arachchi[2], P. S. Russo[3], F. R. Hung[1]
[1]Louisiana State University, Baton Rouge, LA, [2]University of Minnesota, Minneapolis, MN, [3]Georgia Institute of Technology, Atlanta, GA

Hydrophobins are a class of proteins produced by filamentous fungi in soil. Preliminary experiments suggest that these proteins can encapsulate oil in cylindrical ‘blobs’, or gases in cylindrical bubbles, which implies a striking surface activity. These properties, as well as the abundance and ease of biosynthetic manufacture of hydrophobins, suggest that they could be used as ‘natural’ oil spill dispersants. Here we report molecular dynamics (MD) simulations and potential of mean force (PMF) calculations for a class I hydrophobin, EAS, near gas/water and oil/water interfaces. Interfacial properties (free energies, density profiles, radius of gyration and secondary structure of the hydrophobins) that are relevant for the possible use of hydrophobins as ‘natural’ oil dispersants were probed in our simulations using both all-atom and coarse-grained models. The EAS molecules prefer to remain at the interfaces, with the adsorption behavior being strong and irreversible. Significant changes in the radius of gyration and secondary structure of the hydrophobins were observed upon binding to the gas/water and oil/water interfaces. We also performed MD simulations using coarse-grained models where we probed the stability of benzene blobs encapsulated by hydrophobins, with sizes comparable to those realized experimentally by the Russo group. The structures observed in our simulations are not spherical but rather elongated, as indicated by simulation snapshots and measurements of the characteristic dimensions (moments of inertia) of the structures. The stability of the bubbles, as indicated by measurements of the root mean squared deviations (RMSDs) from the initial sizes, is assessed and discussed.

Oil Drop Interactions with Surfaces Varying in Energy and Topography

J. Cremaldi
Tulane University, New Orleans, LA

During an oil spill, oil droplets have the potential to spread on a variety of marine surfaces which may be harmful to living organisms. Biological surfaces represent a range of surface structures and chemistries, both of which affect their interactions with oil droplets. Contact angle measurement represents a method of taking both of these factors into account through measurement of the overall surface activity, and the Cassie-Baxter approximation allows one to model them. In this study, we aim to quantify the interaction of oil with various surfaces, first on flat surfaces of varying wetting properties and then with the added contribution from surface structure. By understanding the type and magnitude of these interactions, our aim is to develop novel oil dispersants (which can be used during an oil spill) that prevent oil droplets from adhering to or contaminating marine life.

Soybean Lecithin as a Dispersant for Crude Oil Spill Applications

E. Nyankson[1], R. B. Gupta[2]
[1]Auburn University, Auburn, AL, [2]Virginia Commonwealth University, Richmond, VA

The traditional chemical dispersant formulations used in combating oil spills are made up of mainly hydrocarbon solvents, petroleum derived surfactants and some additives. The toxicity of these chemical dispersants have necessitated the search for alternative dispersant formulations that are environmentally benign. Soybean lecithin, a well-known surface active agent in the food industry is has excellent emulsification property, it is biodegradable, less toxic and ecologically acceptable. In this study soy bean lecithin was used to formulate dispersants for crude oil spill application. Soybean lecithin was fractionated into phosphatidylinositol (PI) and phosphatidylcholine (PC) enriched fractions. The crude soybean lecithin (CL) and the fractionated PI and PC were solubilized in water and their dispersion effectiveness determined with the U.S EPA's baffled flask test. The dispersion effectiveness of PC was higher than SL (soybean lecithin powder), CL and PI at all the dispersant-to-oil ratios (DORs) tested. However, when the fractionated PI was functionalized and used to formulate the dispersant by solubilizing it in water its dispersion effectiveness improved remarkably and were higher than that of PC. By comparison, it was observed that the dispersion effectiveness of solubilized dioctyl sodium sulfosuccinate (DOSS) and Tween 80 were higher than that of the functionalized PI at lower DORs however at higher DOR the dispersion effectiveness of the functionalized PI was slightly higher than that of solubilized DOSS and Tween 80. The findings from the study suggest that, dispersants formulated from fractionated PI and PC has the potential of replacing traditional dispersant formulations.

The Synthesis of Amphiphilic Polymers Grafted onto Silica Nanoparticles and the Exploration of their Behavior as "Unimolecular Micelle" Dispersants

M. Ejaz[1], A. M. Alb[2], K. Koskowska[2], S. Grayson[2]
[1]Chemistry, Tulane University, New Orleans, LA, [2]Tulane University, New Orleans, LA

The synthesis of amphiphilic polymer grafted silica nanoparticles (AGNs) as critical micelle concentration independent unimolecular micelle dispersants (UMDs) was explored. UMDs are expected to provide a benefit to the affected ecosystem by absorbing and breaking up the oil, without disaggregation under high dilution. The synthesis of AGNs was achieved by grafting biocompatible amphiphilic diblock

polymers shells onto silica nanoparticles cores (SNPC). The grafting of biodegradable and hydrophobic poly(ε-caprolactone) (PCL) was first achieved by surface-initiated ring opening polymerization (SIROP) of CL onto the SNPC. The PCL inner block exhibited OH end groups that were then used either to couple with hydrophilic monomethyl ether carboxyl terminated polyethylene glycol (PEG-COOH) by activated ester coupling or as immobilized macroinitiating sites for further SIROP of glycidol to form a hydrophilic hyperbranched polyglycerol (HPG) block. With these hydrophilic PEG or HPG coronas, AGNs exhibited stable suspensions in water. The AGNs having PCL of different chain length but PEG of the same chain length were also fabricated in order to determine the relation between the amount of PCL and oil encapsulation capacity of these AGNs. The structure and morphology of AGNs were characterized by FTIR, TGA and TEM, etc. 4-Heptylphenol, a UV active hydrocarbon, was used as a model for oil sequestration and it was confirmed that the AGNs can effectively absorb this hydrocarbon from water.

Simulation and Molecular Resolution of Interfacial Characteristics of Water-Squalane-Dispersant Contacts

L. Tan, **L. R. Pratt**
Tulane University, New Orleans, LA

We report on progress on simulation and molecular modeling of the interfacial characteristics of water-squalane-dispersant contacts. Squalane (2,6,10,15,19,23-hexamethyltetracosane) has served as a simulated crude oil for laboratory microtensiometry studies of loading of dispersant materials on water-oil interfaces and the resulting interfacial tensions. A principal interest is a molecular level understanding of the kinetics of adsorption/desorption of surfactants such as SPAN 80 (sorbitan monooleate), and the reversiblility of those processes in view of chain entanglement possibilities. We evaluate the free energies of adsorption/desorption of SPAN 80 with water-squalane interfaces with simulation calculations exploiting parallel tempering and stratification (WHAM) algorithms to achieve enhanced sampling. On the basis of these simulation data, we address a kinetic model for the absorption/desorption processes. We summarize molecular models of electrolyte effects on these phenomena to address the interplay between non-ionic and ionic surfactants, e.g., DOSS (dioctyl sodium sulfosuccinate), in dispersant formulations, in addition to the background electrolyte composition of seawater.

Small Angle X-ray Scattering Studies of Crude Oil in Water with Dispersant

A. Roy, **L. G. Bovenkamp**
Louisiana State University, Baton Rouge, LA

The interaction of hot crude oil with seawater and dispersant at depth involves complex physical and chemical processes. Different fractions of crude oil, defined by molecular weight and solubility, is expected to respond differently during this interaction leading to phase separation, droplet formation, bubble formation, etc. Scattering by light, X-rays and neutrons can be used to study these processes at length scales from nanometers to micrometers. In situ experiments can also be conducted. These techniques also allow measurement without any sample pre-treatment. The present focus of this study is tenths to hundreds of nanometer length scale by small and wide angle X-ray scattering (SAXS and WAXS). A suite of samples from BP's Deepwater Horizon accident was studied by SAXS and WAXS. The samples included emulsified oil, in situ burn residue, tar balls, and riser oil with or without Corexit 9527A. WAXS showed that emulsification or burning lead to expulsion of n-napthene from the heavier

fraction crude oil (mostly asphaltene). Addition of dispersant Corexit and emulsification increased the size of the dominant structure in the riser oil from 0.9 nm, to 2.3 nm to 7.0 nm.

Influence of Particle Roughness and Interfacial Shape on Capillary Forces and Droplet Stabilization

W. He, N. Senbil, A. D. Dinsmore
University of Massachusetts Amherst, Amherst, MA

The behavior of solid particles at fluid interfaces and their ability to stabilize emulsions depend on the particle roughness and the shape of the interface. To understand this dependence, we measure the capillary forces that act on a millimeter-sized particle of defined roughness by monitoring the deflection of a cantilever. We find that particle roughness changes the maximum force and the work needed to remove a particle from the interface. To probe the role of the interface shape, we measure the shape of contact line around a smooth sphere at a cylindrical interface compared to a planar interface. We find that the contact line undulates with a quadrupole component and affects the force to remove the sphere. These results may lead the way to effective particulate-based dispersants by controlling the contact line geometry by particle shape and roughness. This work is supported by the Gulf of Mexico Research Initiative through the C-MEDS consortium.

Characterization Methods for Oil Dispersants

B. Peaden, Z. Zhu, F. Twigg, A. Alb, W. Reed
Tulane University, New Orleans, LA

New agents for oil dispersion are being developed, such as block copolymers and nanoparticle/polymer composites, which will provide single particle, concentration-independent trapping of oil during oil spill remediation efforts. These agents will be ‘volume active’, that is, their capacity to trap oil will depend on their volume, whereas for surfactants, the most common chemical remediation agent, the capacity depends on surface/volume ratio. Here, it is first demonstrated by light scattering that oil trapping by small surfactant micelles is too inefficient to be of use, and hence surfactant oil trapping must be via much larger oil-containing emulsions, which are dynamically unstable and require energy input from the environment to form. Then, several new methods aimed at providing side-to-side characterization of the stability of surfactant and volume-active remediation efforts are introduced; these include ‘filtrodynamics’, which assesses particulate populations via time dependent pressure signals across filters, Simultaneous Multiple Sample Light Scattering (SMSLS), which allows rapid determination of phase diagrams and monitoring of non-equilibrium processes, such as colloidal aggregation. As an adjunct to SMSLS the ability to recognize and count light scattering spikes (LSS) in unstable populations of colloids to produce number concentrations of particles and how these evolve is also under development. Automatic Continuous Mixing has also been valuable in mapping out surfactant/oil/polymer interactions related to oil entrapment. Early results from these methods on commonly used surfactants will be presented. In the near future they will be employed for the polymeric and nanoparticle agents under development.

Stability and Interfacial Adsorption of Hydrophobin Air Bubbles and Oil Blobs

X. Zhang[1], S. Kirby[2], D. Gorman[1], W. Huberty[3], B. Blalock[3], Y. Chen[3], P. Russo[1], L. M. Walker[2], S. L. Anna[2]
[1]Georgia Institute of Technology, Atlanta, GA, [2]Carnegie Mellon University, Pittsburgh, PA, [3]Louisiana State University, Baton Rouge, LA

Cerato-ulmin (CU) is an amphiphilic protein produced by filamentous fungi. Like other members of the abundant hydrophobin class of proteins, it may be considered as a natural Janus particle. Compared to traditional amphiphiles, the globular protein structure, held together by multiple disulfide links, is strong and rigid. These characteristics may account for CU's unusual ability to stabilize cylindrical bubbles and blobs upon encapsulating air and various hydrocarbon-based oils. Surely, hydrophobic proteins and other biomaterials have had a role in cleaning natural oil spills over the millennia; however, an understanding of their abilities in this regard is incomplete. In this work, the dynamic behavior of bubbles and blobs and their stability as a function of time and temperature were studied by simultaneous multi angle dynamic light scattering technique (MADLS). We also evaluate the thickness of CU biofilms using mass balance and image analysis methods. Small-angle X-ray scattering was used to investigate the size and shape of bubbles and blobs, as well as their thickness. To better understand the behavior of CU adsorption/desorption at the air/water or oil/water interface, we used a microtensiometer to measure the dynamic surface tension and elastic modulus.

Surfactant-Mineral-Oil Interactions with Applications in Oil-Spill Dispersion and Clean-up

A. M. Bodratti, M. Tsianou, **P. Alexandridis**
University at Buffalo - The State University of New York, Buffalo, NY

We consider silica nanoparticles in terms of their ability to disperse oil in water. The surface properties of silica are modified by a change in the solution pH and/or the adsorption on the surface of surfactants of the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) family. The physical adsorption of surfactants and the corresponding interactions between silica nanoparticles can be modulated by the addition of displacers such as polar organic solvents, PEO homopolymers, or electrolytes. The connection that we establish between (a) the surfactant organization on the nanoparticle surface and in the bulk solution and (b) macroscopic properties of the dispersions can guide the design of oil-in-water dispersants that incorporate environmentally benign nanoparticles. Such interactions are also central in the ability of surfactants to lift off oil deposited on solid surfaces following an oil spill.

An Integrative Approach to Oil Spill Gelation and Removal using a Hydrophobically Modified Biopolymer in Conjunction with Magnetically Responsive Carbons

P. Venkataraman[1], O. Owoseni[1], S. R. Raghavan[2], A. Bose[3], **V. T. John**[1]
[1]Tulane University, New Orleans, LA, [2]University of Maryland, College Park, MD, [3]University of Rhode Island, Kingston, RI

A new approach for oil spill remediation is described that involves the use of the hydrophobic effect to design an integrative system. Hydrophobically modified high molecular weight chitosan forms an oil-in-water gel at high volume ratios (1:200) of saline water to crude oil. The alkyl chains attached to the

modified chitosan polymer backbone insert into the oil drops through the hydrophobic effect, allowing the polymer to span oil droplets and tether them together to form gel-like aggregates. Sub-micron size carbon microspheres containing magnetite nanoparticles, synthesized from inexpensive precursors such as sucrose and iron chloride using an aerosol based process are introduced into the oil drops to allow the aggregates to respond to external magnetic fields. The method is also applicable to thin layers of crude oil representing surface slicks. Such layers can be corralled and thickened by the application of an oil soluble nonionic surfactant. The addition of hydrophobically modified chitosan allows insertion of the hydrophobes to the thickened oil again forming a gel-like phase. Introduction of the magnetite-carbon particles provides the response needed for oil removal through application of an external magnetic field. The coupled use of the hydrophobic effect and magnetic responsiveness of the system enables applications for confinement, magnetic tracking and easy removal of surface oil.

Session 019: Predicting the Ocean Environment

The Impact of Including Drifter Velocity Observations in the Navy's Assimilation and Forecasting System

S. R. Smith[1], G. Jacobs[1], R. Helber[1], P. Spence[2], M. Carrier[1], H. Ngodock[1]
[1]Naval Research Laboratory, Stennis Space Center, MS, [2]QinetiQ North America, Stennis Space Center, MS

The Navy Coupled Ocean 3D Variational Data Assimilation (NCODA-VAR) system is one of the primary tools that the Navy uses operationally to ingest, process, quality and control, and assimilate ocean observations in near-real time in order to regularly update and improve the forecast skill of several different operational ocean prediction systems. One of the deficiencies of NCODA, however, is its inability to accurately resolve small-scale features. This is primarily because the two predominant sources of data for NCODA are SST and SSH. The spatial resolution of SSH data is typically too coarse to resolve smaller eddies, and SST data lacks the vertical correlation with the subsurface to steer the analysis towards these types of features. The capability to assimilate velocity observations has been added to NCODA by constructing and including additional error covariances to cross-correlate velocity observation with temperature and salinity throughout the water column. Experiments were performed using velocity data inferred and assimilated from 100s of surface drifters that were released during the summer of 2012 in the Northeastern Gulf of Mexico as part of the GoMRI CARTHE drifter experiment. The resulting analyses and forecasts from these experiments are compared with independent observations from altimetry, and temperature and salinity profiles and demonstrate that the inclusion of velocity data assimilation improves the eddy resolution.

Impact of Ocean Velocity Observations Inferred from Lagrangian Drifter Data using the NCOM-4DVAR

M. Carrier[1], H. Ngodock[1], S. Smith[1], P. Muscarella[1], G. Jacobs[1], T. Özgökmen[2], B. Lipphardt[3], B. Haus[2]
[1]Naval Research Laboratory, Stennis Space Ctr., MS, [2]RSMAS - University of Miami, Miami, FL, [3]University of Delaware, Newark, DE

Eulerian velocity observations are derived from 300 drifters released in the Gulf of Mexico by The Consortium for Advanced Research on Transport of Hydrocarbon in the Environment (CARTHE) during

the summer 2012 Grand Lagrangian Deployment (GLAD) experiment. These data are directly assimilated into the NCOM four-dimensional variational (4DVAR) analysis system. The assimilation experiments take advantage of the velocity data along with in-situ and satellite measurements of temperature and salinity. Three different experiments are done: (i) A non-assimilative NCOM free-run, (ii) an assimilative NCOM run that utilizes temperature and salinity observations, and (iii) an assimilative NCOM run that uses all observations including the GLAD velocities. The resulting analyses and subsequent forecasts are compared to assimilated and future GLAD velocity and temperature/salinity observations to determine the performance of each experiment and the impact of the GLAD data on the analysis and forecast. It is found that the GLAD velocity data greatly improves the characterization of the circulation, with the forecast showing a better fit to future GLAD observations than those experiments without the velocity data included.