MOSSFA
MARINE OIL SNOW SEDIMENTATION
& FLOCCULENT ACCUMULATION

Gulf of Mexico Research Initiative Synthesis Workshop I
MOSSFA – Core Area Two

November 26-28, 2018
Galveston, Texas

Facilitated and Organized by:

ADDOMEx
(Aggregation and Degradation of Dispersants and Oil by Microbial Exopolymers)

C-IMAGE
(Center for the Integrated Modeling and Analysis of Gulf Ecosystems)

EXECUTIVE SUMMARY

The MOSSFA Workshop Steering Committee (SC), consisting of Dr. Antonietta Quigg (ADDOMEx and Co-Chair), Dr. David Hollander (C-IMAGE and Co-Chair), Dr. Adrian Burd (RFP-IV) and Dr. Jeffrey Chanton (C-IMAGE), met over a period of 3 months to develop the goals and agenda for the workshop. The total number of workshop attendees was 46 and they included researchers from academia, mostly from GoMRI-funded centers (C-IMAGE, ADDOMEx, ECOGIG, DEEP-C, CARTHE, DEEPEND, DROPPS, CSOMIO, and recipients of RFP-V and RFP-VI awards), representatives from industry that are focused on oil spill response, and federal agency researchers focused on modeling and damage assessment. The meeting was streamed live for those who could not attend in person and accessed through the Texas A&M University at Galveston Information and Technology portal.

The goals of the workshop were consistent with other GoMRI Synthesis Workshops, to collect and integrate key findings over the previous eight years of GoMRI-funded research. The workshop was divided into four focus groups, each addressing one aspect of the MOSSFA process: (1) Formation, (2) Sedimentation, (3) Modeling and (4) Oil Spill Response, NRDA and Restoration. Each focus group began with three to five overview presentations followed by breakout group to discussed the key concepts put forth in each session and identified the knowledge gaps based on their collective expertise. A series of key questions were then assembled and grouped based on session and discussed. In response to the current state-of-knowledge and advanced understanding of the MOSSFA phenomena and in support of the GoMRI Synthesis and Legacy team task 2 focused on oil fate, the MOSSFA steering committee put forward the goal of authoring two scientific publications. The first paper will focus on the mechanisms of MOS formation, its sedimentation and the state-of-the science for modeling and prediction of MOSSFA events. The second paper will focus on how the MOSSFA phenomenon can be applied to oil spill emergency response, used to inform and complement the NRDA process and identify environmental and biological restoration projects. The second paper will also address the frontier perspectives of shallow water MOSSFA events in coastal marine and estuarine settings and in freshwater (rivers and lakes) environments.

ACKNOWLEDGEMENTS

The agenda, participant list, breakout themes, and discussions were developed with thoughtful input from the Steering Committee: Dr. Antonietta Quigg (ADDOMEx), Dr. Adrian Burd (FOMOSA, RFP-IV), Dr. David Hollander (C-IMAGE), and Dr. Jeffrey Chanton (C-IMAGE). Considerable support was also provided by Ms. Sherryl Gilbert and Mr. Benjamin Prueitt (C-IMAGE). The workshop was funded by the Gulf of Mexico Research Initiative (GoMRI) though a supplemental working group award with partial support from each collaborating center and the Gulf of Mexico Alliance (GOMA). These organizers would also like to thank Noah Claflin, Jennifer Genzer, Patricia (Patty) Gonzales, Jessica Hillhouse, Manoj Kamalanathan and Rachel Windham for their on-site meeting support at Texas A&M University at Galveston.

DEFINITIONS

OMA – oil mineral aggregates

OSA – oil suspended particulate matter aggregate

OPA – oil particle aggregates

MOS – marine oil snow

MOSSFA – marine oil snow sedimentation and flocculent accumulation

SPM – suspended particulate matter

ORMS – oil related marine snow

WAF – water accommodated fraction

CEWAF – chemically enhanced water accommodated fraction, likely enhanced by a surfactant

EPS – extracellular polymeric substances

BACKGROUND/HISTORY

In the wake of the *Deepwater Horizon* oil spill in 2010, researchers discovered that a significant fraction of the oil (14%) was transported to the deep ocean associated with marine snow. In 2013, the University of South Florida received a supplemental grant from the Gulf of Mexico Research Initiative (GoMRI) to establish a Marine Oil Snow Sedimentation and Flocculent Accumulation (MOSSFA) working group during the RFP-I award period (2011-2014). The main objectives for the group were to investigate the following: (1) factors affecting the formation and sinking of MOS (marine oil snow) in the water column, (2) the deposition, accumulation, and biogeochemical fate of MOS on the seafloor, and (3) the ecologic impacts of MOS on pelagic and benthic species and communities. The chair and co-chairs of the initial MOSSFA working group were Uta Passow (ECOGIG) as Chair; Kendra Daly (C-IMAGE), Jeff Chanton (Deep-C and ECOGIG) and David Hollander (C-IMAGE and Deep-C) as co-Chairs; and Nancy Kinner (UNH-Center for Spills in the Environment) as the Working Group facilitator.

Over the course of RFP-I to RFP-V, the working group has arranged five MOSSFA themed gatherings;

1. 2013 MOSSFA Workshop, Tallahassee in October 22-23, 2013 (report provided at http://deep-c.org/mossfa),
2. 2014 MOSSFA Town Hall, Mobile, AL, coinciding with the 2014 GoMOSES conference
3. 2017 MOSSFA Meeting, New Orleans, LA, coinciding with the 2017 GoMOSES conference (February 6, 2017)
4. 2017 Report Writing Workshop, St. Petersburg, FL, 30 March 30, 2017
5. 2018 Organizing Committee Meeting, New Orleans, LA, coinciding with the 2018 GoMOSES conference.

The aforementioned efforts resulted in a linked, focused and comprehensive team of researchers focused on all stages of the MOSSFA continuum, from formation to deposition. The various workshops provided a venue with consistent opportunities for sharing results to date and to discuss ongoing field and laboratory efforts.

The invitees to the Galveston workshop were selected based on their affiliation and research background. The attendee list included researchers from academia, mostly from GoMRI funded centers, representatives from industry that are focused on oil spill response, and federal agency researchers focused on modeling and damage assessment. The steering committee also extended invitations to non-US entities to provide an international picture of MOSSFA related risk and impacts. The total number of attendees was 46, including researchers from the consortia C-IMAGE, ADDOMEx, ECOGIG, DEEP-C, CARTHE, DEEPEND, DROPPS, CSOMIO, and recipients of RFP-V and RFP-VI awards. The meeting was streamed live for those who could not attend in person and accessed through the TAMU-Galveston Information and Technology portal.

The goals of the workshop were consistent with other GoMRI Synthesis Workshops, to collect and integrate key findings over the previous eight years of GoMRI-funded research. The workshop was divided into four themes of work, each focusing on one aspect of the MOSSFA process: (1) Formation, (2) Sedimentation, (3) Modeling and (4) Response/Restoration. Each theme began with three to five overview presentations. After the presentations, participants were divided up into four breakout groups to discuss and prioritize knowledge gaps. Each of the breakout groups were assigned a facilitator and rapporteur.

Each breakout group discussed the key concepts put forth in each session and identified the knowledge gaps based on their collective expertise. The questions were then grouped based on session and discussed.

This workshop report briefly summarizes each presentation and lists the priority research gaps for each session. Some of the presentations along with other meeting items can be publicly accessed at:

https://www.marine.usf.edu/c-image/component/k2/gomri-synthesis-workshop-mossfa-2018

Not all presentations are available as some contain sensitive non-published research.

I. SESSION 1: MOSSFA FORMATION (DR. PETER SANTSCHI, FACILITATOR)

The Formation Session began with a presentation from **Dr. Uta Passow** from Memorial University of Newfoundland who is a member of the ADDOMEx and ECOGIG consortia and a recipient of a small investigator RFP-V grant. Dr. Passow provided participants with an overview of marine oil snow (MOS) formation and composition.

General Concepts: MOS is made up of particle-oil associations composed of any combinations of oil, minerals, sediment and bacteria. These oil particle associations can be categorized based on their makeup and size: (1) OMAs, OSAs, OPAs and oil-SPM (defined above, page 2) are small (<10µm) droplets, solids or flakes that are coated with mineral grains and have a relatively slow sinking velocity of less than 10 mm/s, (2) MOS or ORMS are formed via aggregation/coagulation or biological production and are relatively large in size (>500µm) with a higher sinking velocity of hundreds of meters per day and (3) bacteria-oil-agglomerations that are produced by microbial response to oil exposure. Both microbial oil snow, which forms because of oil contamination, and natural marine snow that inadvertently incorporates oil, may act as a transport vehicle for oil compounds, rapidly transferring oil residues to the seafloor in depths greater than 1400m. The presence of oil does not lead to reduced sinking velocities (Figure 1).

Role of Corexit: The interactions between oil or oil + Corexit with marine snow (biologically mediated process) are extremely complex. However, experiments have revealed some general rules that make this process potentially predictable if one considers the "ecosystem state". Corexit can disperse both oil and the exopolymeric substances that play an important role for marine snow formation. Corexit may inhibit MOS formation. The amount of oil incorporated into MOS depends on the concentrations of both, oil and marine snow (linear

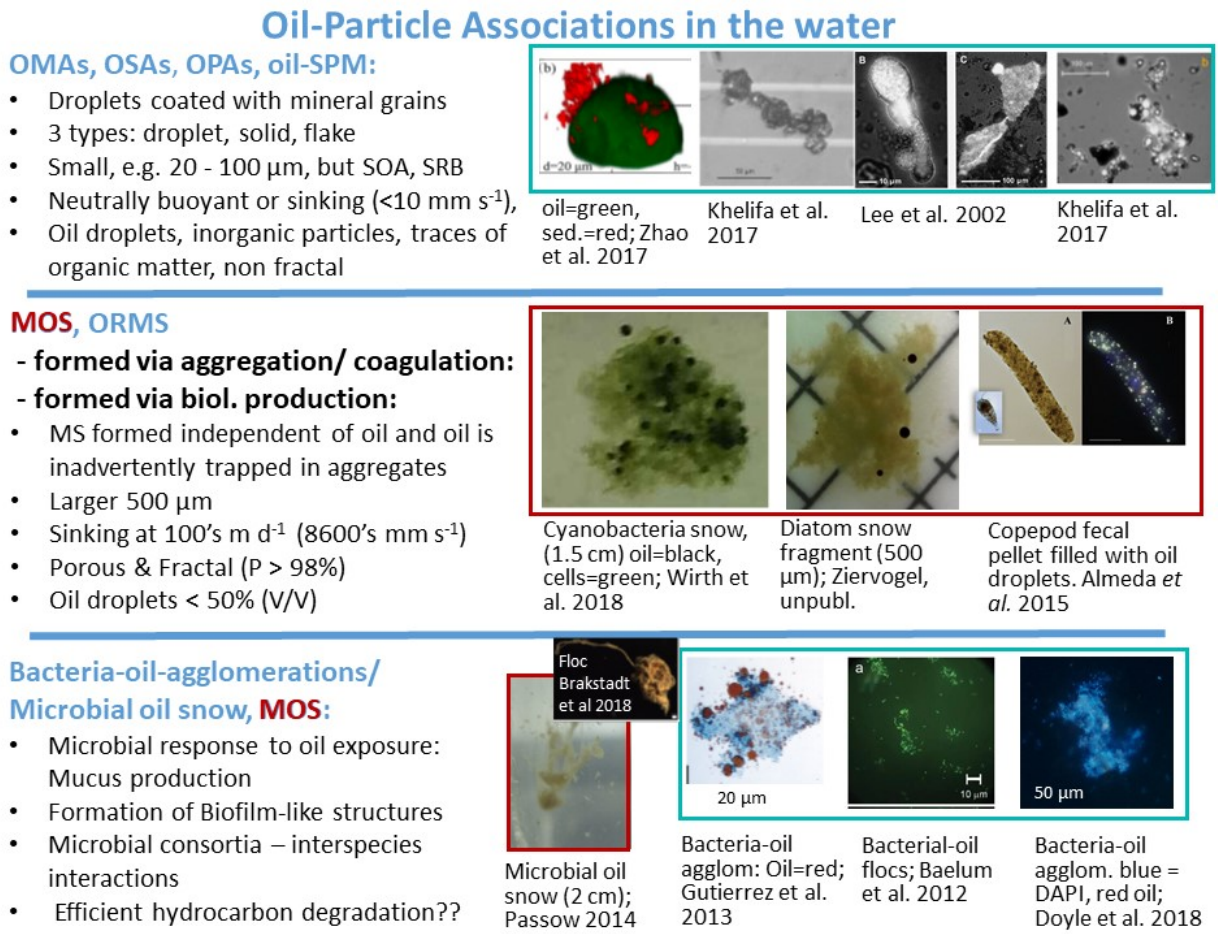

Figure 1. Summary of definitions and characteristics of different oil/particle interactions.

function). Oil compounds are incorporated into marine snow as droplets and also sorbed onto cells. Physico-chemical properties of oil compounds largely determine the partitioning: Droplet incorporation is proportional to droplet concentration whereas sorption is proportional to the aqueous concentration. Droplet incorporation is immediate, sorption takes > 1 day. The relative timing of the encounter between marine snow, oil, and dispersant are essential in determining the formation of MOS and the incorporation of oil compounds into sinking MOS, but should be principally predictable. Biodegradation enhanced in MOS compared to dispersed or dissolved oil

Dr. Chen Xu from Texas A&M University at Galveston followed with a presentation that provided more detail on the role of Corexit on MOS formation by summarizing experiments conducted on baffled recirculating tanks at the Geochemical and Environmental Research Group (GERG) in College Station, Texas (Figure 2).

Role of Corexit in Mesocosm Studies: Experiments in the tanks (with a dispersant:oil ratio (DOR) of 1:20) showed that WAF stimulated extracellular polysaccharide production and that CEWAF stimulated both EPS and protein production. This increase in exudate production increased the amount of aggregates, however, they exhibited a decrease in sinking velocities. The association of oil and dispersant with the EPS increased aggregate buoyancy.

Tanks with Corexit only inhibited EPS formation. Oil-dispersant exudates have a different composition than natural exudates;
Protein-C/carbohydrate-C ratio is an important factor that regulates EPS aggregation and interaction with oil and dispersant.

Effects of Phytoplankon/Photodegradation: Microbial diversity increased with WAF, phytoplankton responses are species specific. Biological degradation is responsible for most of the degradation as opposed to photodegradation. Responses are species-specific; microbial community diversity and structure differed dependent on if dispersant is used.

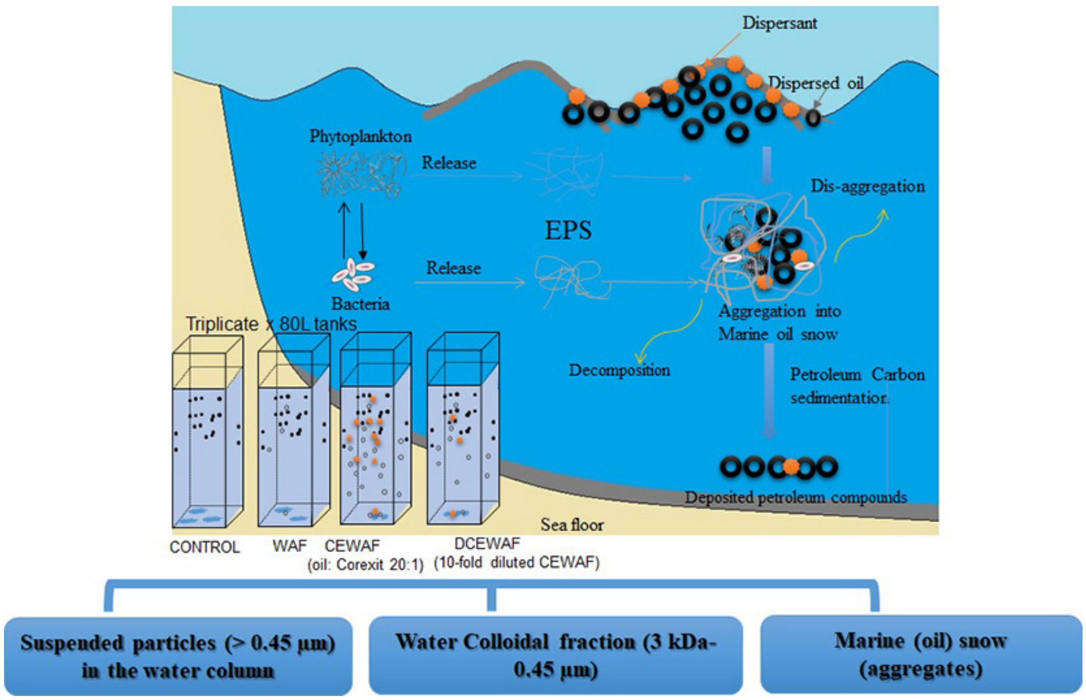

Figure 2. This summary figure shows the graphical representation of the baffled recirculating tanks with different treatments (Xu et al. 2018)

Dr. Kai Ziervogel (University of New Hampshire, ECOGIG) presented information on the role of microbial interactions on MOS formation and transport.

Microbes and MOS: Microbes – and more precisely hydrocarbon-degrading bacteria – play a key role in the fate of oil in the ocean. If we want to talk about how microbes affect MOS formation, then we need to consider some of the processes that are involved in the microbial oil degradation network illustrated here in this schematic by Head et al. (2006) (Figure 3). Oil-degrading microbes trigger MOS formation in a two-step process:

1. Formation: First, the formation of 'cellular flocs' is the result of a physiological mechanism for oil degrading microbes (e.g. Bælum et al. 2012). The flocs are oil degradation products. The surfactants produced by oil-degrading bacteria (EPS) are important as they enhance the solubility of hydrocarbons and thus their bioavailabilty. The microbes build from a biofilm around oil droplets.

2. Transport: These ‘cellular flocs’ grow and sink (e.g. Kleindienst et al. 2015). The EPS ballast material is trapped in mucus matrix (e.g. Ziervogel et al. 2012). Microbial communities that grow on MOS in deep water are less diverse compared to surface water MOS. Microbial activities on MOS (including secondary consumers) affects elemental fluxes in the water column. Water collected from an oil slick in May 2010 exhibited production of EPS by microbes degrading oil after one week. Over time, the natural particles that were incorporated in mucus fell off surface slick and sank, evidenced by the presence of planktonic cells in sediment material.

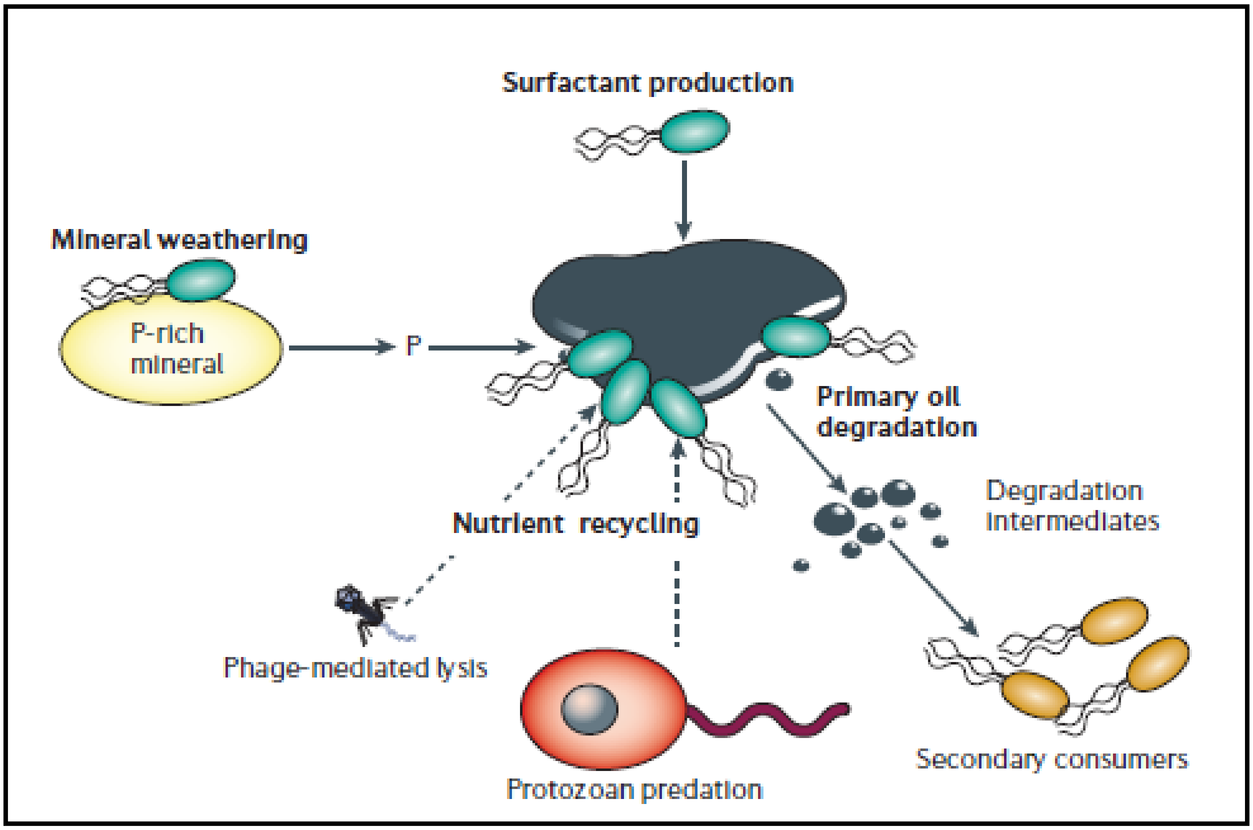

Figure 3. Role of microbes in biodegradation and MOS formation (Head et al. 2006)

Microbes, MOS and Corexit: Cellular flocs formed with and w/o Corexit (Bælum et al. 2012; Doyle et al. 2018). Microbial MOS in deep waters formed with and w/o Corexit and nutrients (Kleindienst et al. 2015).

Dr. Ali Khelifa from the Bedford Institute of Oceanography spoke about OSA formation and modelling.

OSA formation: Surface droplets become entrained and interact with suspended particles (not sediment) and aggregate together; it is a natural process. Minerals do not need to be present for OSA formation. The effect of OSA is in sending oil from surface to bottom. Present knowledge is summarized by CRRC – physical transport and chemical behavior. July 2017 section on OSA formation. https://crrc.unh.edu/dispersant_science

Primary particles fall and grow bigger as they sink, sinking faster. That happens in oil droplets in this process. Sediment floc attached to oil droplet –List of favorable conditions for OSA formation (concentration of SPM, oil, polar content in oil, relative motion, ionic strength, high temperature, chemical dispersant) (and non favorable); In offshore we don't have high sediment concentration, but we have particles.
Salt helps droplets aggregate together.

A. Formation Breakout Session Discussion Summary

Oil affects the formation and fate of MOS directly and indirectly through affecting the buoyancy of particles and their stickiness (which affects their formation rate), and predictions of MOS formation depend on these and additional factors such as particle density, porosity, and concentration. The difficulty with making quantitative predictions is that models will have to integrate small-scale chemistry with large scale phenomena such as phytoplankton blooms. As an example, the protein to polysaccharide ratio, or alternatively the C/N ratio, may be useful in predicting stickiness (and hence MOS formation) knowing the large-scale oil, phytoplankton, and microbial spatial and temporal distributions. There are also experimental issues with understanding the dynamics of oil and MOS across the range of naturally occurring sizes. For example, image analysis cannot characterize all the relevant shape=-parameters of the particles, and for micro-particles there are issues with standard techniques such as staining and filtration (especially for gel particles). Successful modeling approaches will be crucial for incorporating MOSSFA into emergency response, prediction, and damage assessment activities.

The fate and distribution of MOSSFA resulting from MOS formation remains largely an unanswered question. For example, it is unclear how and whether MOS enters the food chain (e.g. by zooplankton grazing), and if does what are its effects. In addition, zooplankton grazing will affect MOS size distributions, but experiments to determine these impacts are hard to do.

The role of dispersants on MOS formation also remains unclear.

B. Prioritized Questions from Formation Breakout Discussions

- Can we predict physical properties of MOS, oil effects on MOS formation rates/properties, effects of dispersant on MOS formation?
- Do dispersants enhance or impede oil particle formation or MOS formation and sinking?
- Can MOSSFA formation be manipulated?
- What is the importance of biological and lithogenic characteristics in MOS formation?
- Would we have a MOSSFA event without the Mississippi River? How much did Mississippi River contribute to MS and MOS formation?
- What is timing of events for MOS to form? Rate? And what conditions contribute to MOS formation? Aka what is trigger?
- Is protein: carb ratio a good predictor for stickiness of EPS/MS/MOS?
- Is marine snow environmentally relevant?
- How do you predict the concentration in space and time of MOS?
- Can we use the protein/carbohydrate ratio to predict stickiness?

- Can we address which EPS is produced by phytoplankton or bacteria, and if it comprises of oil derived carbon?
- Can we use OPA (oil particulate aggregates) as an overall term for OMAs (OSAs, Oil-SPM, etc.)? The community needs a standardized nomenclature.
- Can OPA lead to BOA (Bacterial Oil Agglomerations)? Then to MS? Is there a continuum/life cycle?
- Can the community classify these acronyms by formation process? Size? Density or sinking velocity?
- The role of fungi is important and currently unanswered
- MOS produced by phytoplankton, bacteria, fungi, inorganics, photodegradation
- How much enhancement of marine snow occurred because of oil?
- Need conceptual models for MOSSFA formation

II. SESSION 2 - MOSSFA SEDIMENTATION (DR. JEFFREY CHANTON, CHAIR)

Dr. Isabel Romero from the University of South Florida discussed the various components of hydrocarbons in the sediment, and the possible transformation processes that created them.

The objectives were to: (1) discuss the role of transformation processes (UV light, evaporation) and new sources of materials (e.g., black carbon, drilling mud, clay) on sedimentation, (2) examine the extent and processes impacting sedimentation of oil-derived material (MOS/OMAS), (3) review the role of surface and depth oil-derived material (MOS/OMAS) to the sedimentation of oil, and (4) discuss the processes impacting oil-derived material (MOS/OMAS) on the seafloor after 3-years (DWH) to 37 years (Ixtoc 1) (e.g., degradation, transformation, resuspension/re-distribution).

Spatial distribution of oil residues: For the spatial distribution model we used interpolation analysis of 1,798 sites (Empirical Bayesian Kriging, Arc-GIS, Figure 4). We found post-spill deposition of oil-derived material in 110,000 km^2, approximately 56% of the studied area (hydrocarbon inputs corrected by background concentrations). Calculations for the total deposition are 21± 10% (up to 47%) (~0.8 – 1.8 million barrels) of the total amount of oil discharged and not recovered from the DWH. Concentration of hydrocarbon mixtures in sediment are not explained by different source oils or by weathering levels and evidence points to vertical transport for deposition (MOS/OMAS). 99% of the deep-sea area contains hydrocarbons from the surface; however, larger amounts of oil residues were from depth (~40,000-74,000 barrels), followed by residues from the surface (~35,000-64,000 barrels) and from the submerged plumes (760-1,400 barrels).

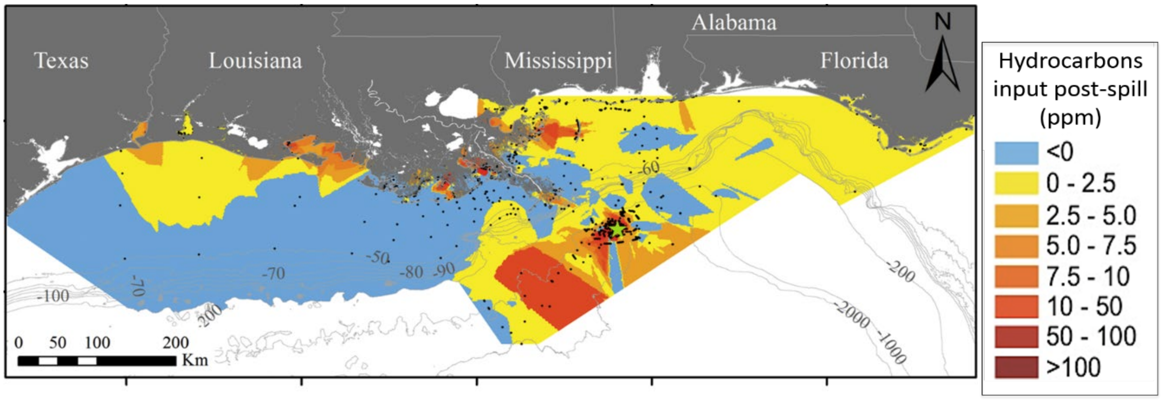

Figure 4. Spatial distribution model of residual hydrocarbon concentrations from coastal to deep-sea areas. Data was interpolated using Empirical Bayesian Kriging (EBK) analysis to calculate cumulative areal extent for each concentration range. From Romero et al. (2017)

Research Gaps:
1- Role of transformation processes (photoxidation, biodegradation, dissolution) on oxidation products
2- Spatial extent (coastal-deep-sea) of oxidation products generated from deposited oil residues
3- Role of oil residue chemical composition on generation of oxidation products

Dr. Patrick Schwing presented on the benthic biological impacts and response of oil deposition in both the northern (DWH) and southern (Ixtoc 1) Gulf of Mexico.

The deep benthos: The *Deepwater Horizon* well site is in zone of high benthic species richness. There are two main groups of benthic species: (1) Macrofauna (medium size) >0.3 mm (2) Meiofauna (small size) >0.044 mm and <0.3 mm. The main species used for assessing benthic health is foraminifera for the following reasons; Short lifespan-months to years (community turnover, density/diversity), Heterotrophic (changing carbon sources, stable C-isotopes), Preservation of environmental change in shells (tests), High concentrations in cores (Statistically robust). Much of the deposition occurred directly adjacent to the wellhead in the Mississippi Canyon and in the Desoto Canyon. We found 80-93% decrease in density, 33-40% decrease in diversity, and could be related to increase in petroleum compounds and reducing conditions (Figure 5).

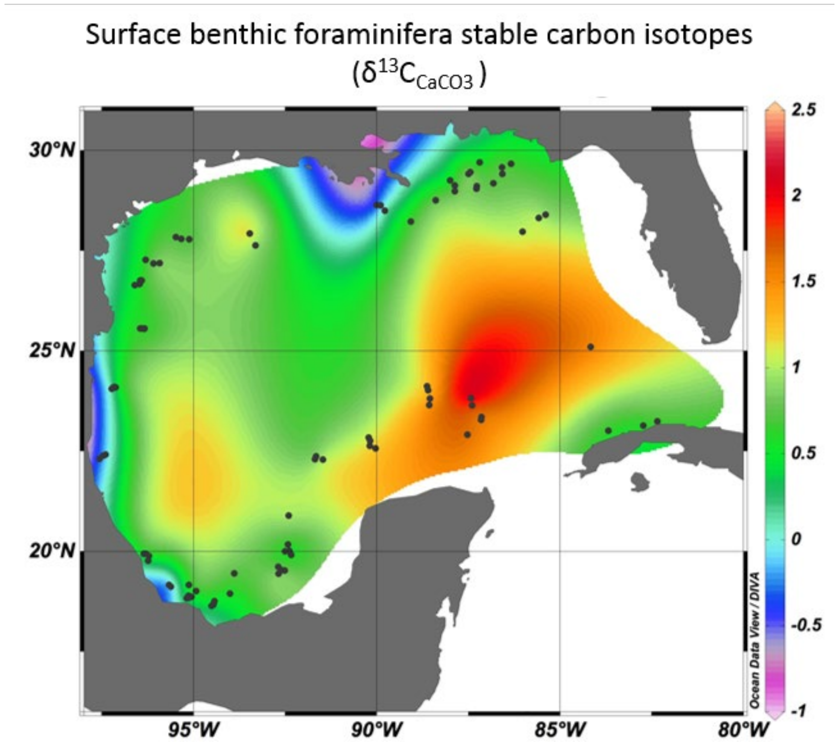

Figure 5. DIVA-gridded baseline map of surface sediment benthic foraminifera (Cibicidoides pachyderma and C. wuellerstorfi) stable carbon isotope composition (δ13C). The stable carbon isotope composition of benthic foraminifera has proven to be a sensitive tracer for the occurrence and extent of MOSSFA. This map serves as a baseline from which any future impacts from MOSSFA can be quantitatively characterized.

Research Gaps we Filled:
Spatial extent of MOSSFA

- NGOM (DWH): 8,400-35,425 km^2 (Centered near DWH wellhead, Mississippi & Desoto Canyons)
- SGOM (Ixtoc 1): 6,347-53,129 km^2
- High end agrees with sea surface extent (75,000 km^2)
- Biological impact and response (NGOM, SGOM)
- 80-93% decrease in density, 30-40% decrease in diversity
- 3-5 years to return to steady state

Dr. Mead Allison presented on the factors that may influence river-derived particle availability for marine oil snow production.

Role of MS River: During the DWH, much was discussed on the role of the Mississippi river in contributing to the physical oceanography as well as its role in providing particulates for oil deposition to the shelf, or offshore with oil interaction in river plumes. Time scales of particle movement are very different. Even in freshwater systems, particles are in flocculant form, so when the sediment reaches the estuary, it is already in flocculant form. High sediment output is found in areas of low discharge due to greening of river. High variability of particulate concentrations in northern Gulf. Need to consider all regions. Events can both remove particulates from Gulf and deposit them downslope. Shelf resuspension also plays a role. Only some correlation between discharge and sediment load.

Dr. Bekka Larson presented on MOSSFA's contribution to both sedimentation and accumulation, and provided a summary on how these things are qualitatively and quantitatively different.

Baseline Needs: Sedimentation does not always lead to accumulation. Sedimentation occurs on shorter time scales and accumulation on longer time scales. MOSSFA is an event, and focuses on what is a deviation from the normal state. To that end, we need to understand natural sedimentation patters (baseline data, Figure 6)). Thorium 234 can give sedimentation on monthly time scales. Sedimentation rate decreased after depositional pulse. We have the data to inform what the normal state is.

Gaps: Remobilization can reintroduce MOSSFA to ecosystem via downslope transport. Lead 210 is more for longer term studies. What is the ultimate fate and sequestration?

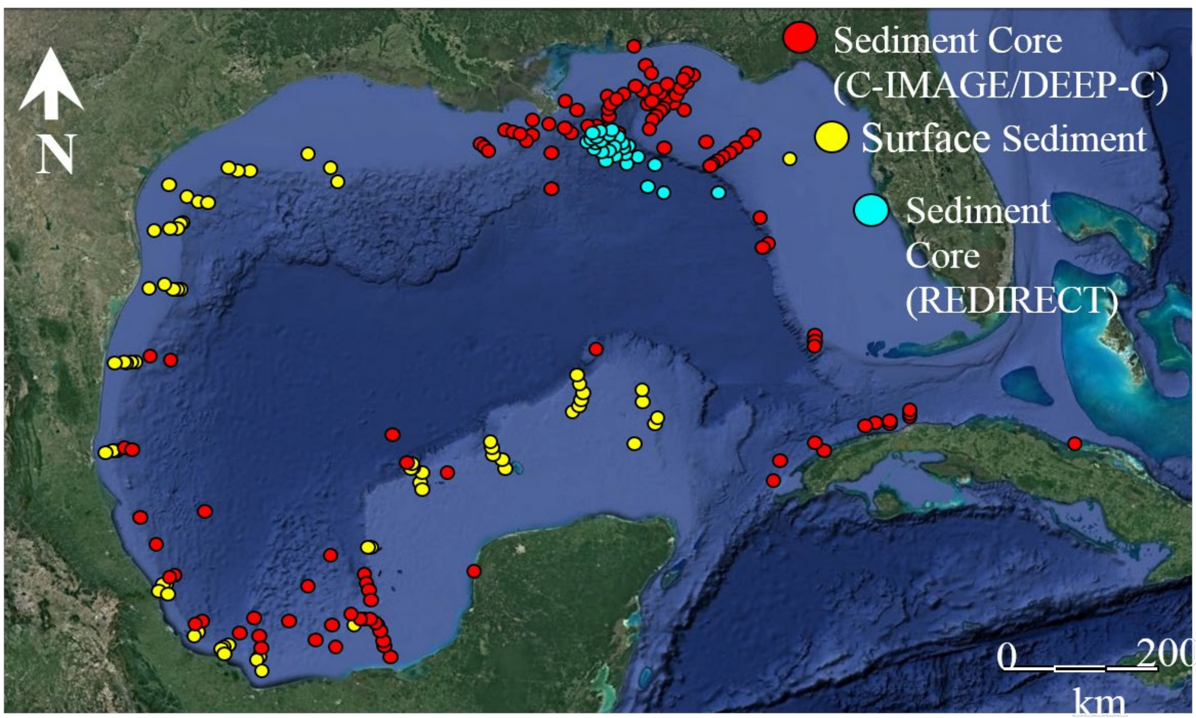

Figure 6. Map of all collected sediments across C-IMAGE, DEEP-C, and REDIRECT cruises.

Dr. Arne Diercks from the University of Southern Mississippi is associated with the ECOGIG consortium and the RFP-VI REDIRECT project (Resuspension, Redistribution and Deposition of DWH Recalcitrant Hydrocarbons to Offshore Depocenters). His presentation focused on the concept of "Secondhand" MOSSFA and how currents and morphology can impact the ultimate fate of MOSSFA. The initial assessment of marine-oil sedimentation did not include the concept of resuspension through the nepheloid layer.

Sediment Traps: Our researchers used a vertical array of instrumentation over very short time scales, looking at the ratios of POC between traps at the top and bottom of the water column to detect resuspension events. Re-suspension events were characterized within sediment trap samples by comparing the POC content with sample dry weight and also the lithogenic silica (LSi) flux. The ratio of POC to Sample Dry Weight was identified as an indicator for material collected in the sediment traps originating from resuspension events. Larger more far field suspension is seen in both traps and the per day flux changes with current direction. This second hand resuspension of MOFFA is impacting corals and other deep sea biota.

Take Home Messaging: We know we have resuspension events remobilize material from the seafloor in the area of the initial deposition of the MOSSFA event. We also have data that support the redistribution. We have indication from an independent study (Charles Fisher's group) that point to a potential secondhand exposure of corals near MC344. We have a large area of seafloor >87% in our study area, that has small slope gradients and an intricate drainage system that is receiving remobilized material from the high energy slopes in the area of the oil spill. Too early to say what the final outcome of the redistribution of the secondhand MOSSFA will be, but preliminary data do show that we have redistribution of this material in our core samples collected to the SE of the DWH site.

A. Sedimentation Breakout Session Discussion Summary

Questions and contradictory ideas were raised concerning the geographical scale of MOSSFA impacts on the sediments and the nature of the oil-derived material they contain as they reach the seafloor. For example, there were contradictory views expressed on the toxicity of the petrocarbon carried to the seafloor by MOSSFA events. In spite of this, there was broad consensus about other gaps in our understanding. For example, the relative roles of phytoplankton (e.g. diatoms) and mineral particles in providing ballast for sinking MOS particles remains unclear, as does the role of biodegradation and food-web interactions in affecting the density of MOS particles and their concentrations as they sink through the water column.

The spatial distribution of MOSSFA impacts on the seafloor was and important question, especially when considering trade-offs in devising response strategies in an emergency situation. For example, significant smothering of benthic habitat may need to be considered as it would affect environmental restoration post-spill.

B. Prioritized Questions from Sedimentation Breakout Discussions

- What is the spatial/temporal distribution of MOS? Can we incorporate bioscavenging in the ecosystem model? Is resuspension important and if so, on what temporal or spatial scales?
- What is the stability of large MOSSFA particles in terms of turbulence?
- What is the role of oil degradation (and densification) on enhancing (or attenuating) sinking velocity? (as a particle sinks and the oil associated with it is continually degraded)
- Does the water column standing stock of carbonate particles or lithogenic particles relative to the amount of material deposited on the sea floor vary during the MOSSFA

event? Eg. How many water column inventories were stripped during the MOSSFA event?

- How benign is petrocarbon on the seafloor in terms of causing anoxia and or toxicity?
- What is the role of minerals in sinking of marine oil snow?
- How do MOS sinking velocities vary with density? Does this change with depth, oil amount, size, shape, fragmentation and water column energy?
- What is the long term fate of petrocarbon on the seafloor?
- Are *in situ* sinking rates higher than those seen in lab experiments?
    - What is the effect of grazing?
    - Is the sinking too fast for oil to be degraded in MOS compared to MS?
- What particles cause ballast?
- Stability of marine snow in addition to formation/fate of the oil

III. SESSION 3: MOSSFA MODELING (DR. ADRIAN BURD, CHAIR)

Dr. Chris Barker with NOAA's Office of Response and Restoration discussed the current state of oil spill fate and transport modeling in practice (Figure 7).

Role of Response: The response team initially is focused on the "actionable". NOAA's Science Support Team provides overflights, trajectory predictions, threat assessment, toxicity assessment, weather predictions, data on currents, consultation /problem solving, information management and coordinates to NOAA's Incident Response Partnership with the U.S. Coast Guard to maintain integrated Scientific Support Teams. The office uses tools that are quick to initialize and run since they need to ingest all available data and to be as flexible as possible. Follow up questions focus on the injury assessment 'what happened to the oil?' And what did it injure? These questions can take months to years to answer, and emphasize the importance of baseline data. During DWH, we didn't have direct concentrations of oil at the blowout site, and for modeling that is key.

Models: Currently all models use a Lagrangian approach that has no grid size dependence, preserves sharp gradients, and allow the addition of "behavior" to particles. Slicks can be tracked and predicted with 2-d model, but droplets in the subsurface needs 3-D and droplet size distribution (DSD) is key. Models can incorporate "pseudo components" that have attributes that reflect a range of similar compounds (boiling point is key to predict evaporation) solubility, degradation constant.

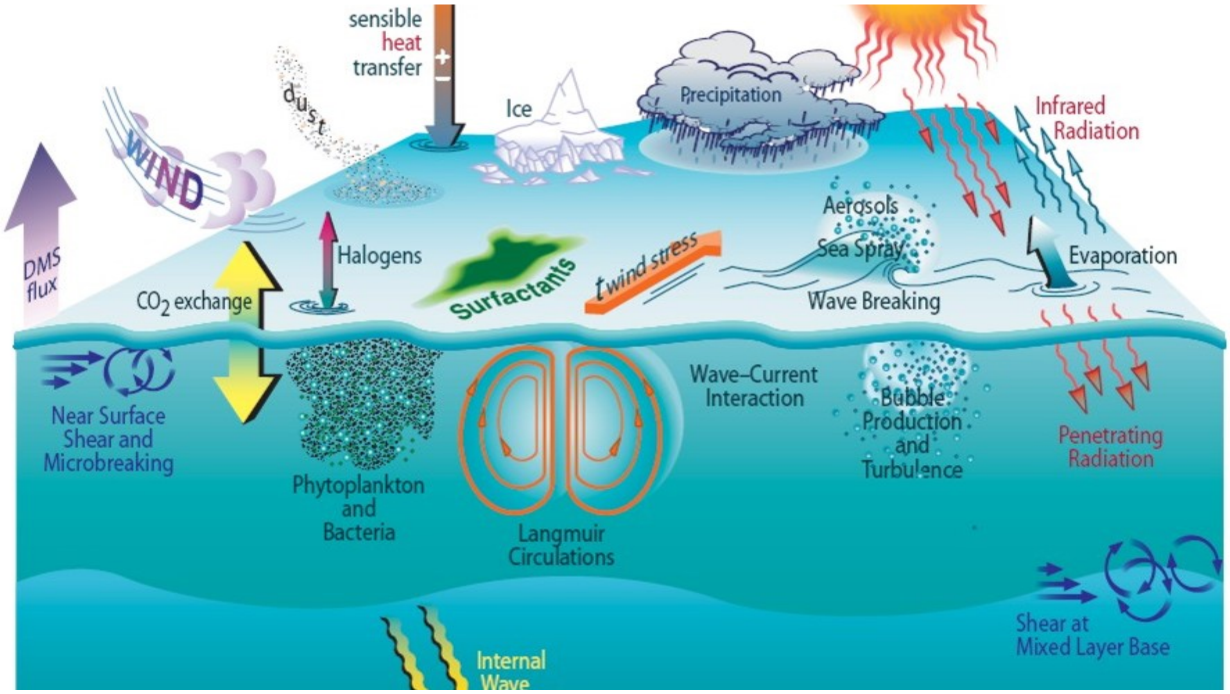

Figure 7. Physical ocean forces and biological interaction. Image courtesy of Jayne Doucette (WHOI). Modeling inputs for oil spill tracking.

Dr. Anusha Dissanayake with RPS Ocean Science discussed the recent developments in numerical modeling post DWH.

Current Catalog of Models: Current models are CDOG - Comprehensive Deepwater Oil and Gas Blowout Model – Clarkson University, Potsdam NY by Yapa et al. SIMAP/OILMAP - Integrated Oil Spill Impact Model System/Oil Spill Model and Response System - Models at RPS Ocean Science (ASA) in Rhode Island by French McCay et al. and Spaulding et al. OSCAR - Oil Spill Contingency and Response Model at SINTEF Norway - Reed et al. GNOME - General NOAA Operational Modeling Environment - Model at NOAA Bill Lehr, Chris Barker and CJ Beegle Krause TAMOC - Texas A&M Oil Spill (Outfalls) Calculator by Socolofsky et al. CMS - Connectivity Modeling System - Paris et al. LTRANS - Lagrangian TRANSport model - North et al. BLOSOM – The National Energy Technology Laboratory (NETL) Blowout and Spill Occurrence Model MOHID – Water Modeling System – Portugal

Near/Far Field: Model development and integration occurs in different steps, first focus on the near field and then move to the far field. In the near field, there is bubble and droplet breakup, physical and chemical processes of bubble and droplet interactions. The far field can include how the bubbles droplets interact with land in addition to the forces acting upon the bubbles and droplets. Items to incorporate are the heat and mass transfer of bubbles and droplets. MOSSFA modeling will include settling fluxes and a stickiness factor. We've incorporated an aggregation model that factors in fractal scaling, porosity, aggregate size and density and terminal velocity with different collision mechanisms (Brownian, Fluid shear, differential settling).

Improvements: There have been new developments/improvements in oil spill models after DWH in the near field, far-field, bubble and droplet break-up models. The formation of MOS can be added as an extension to the oil and suspended particle aggregation or oil mineral aggregation in the coastal environments. Determining how to define input variables for these models is important. Experimental and modeling groups should communicate with each other. Future modifications for marine oil snow formation models include the temporal evolution of oil and MOS in the water column and coupling the model with a hydrodynamic model that will allow us to simulate oil and MOS advected within a system. Modelers require additional research on the factors controlling aggregate fractal structure, stickiness, and disaggregation rates to improve the model predictions and comparison with data. We also need information on the biodegradation of oil in MOS aggregates. We can use the protein/carbohydrate ratio as a predictor of stickiness and aggregation potential.

Drs Ken Lee and Michel Boufadel shared their allotted time to discuss the significance of oil particle interactions in oil spill response. Dr. Ken Lee is with the Department of Fisheries and Oceans Canada (DFO) and Dr. Michel Boufadel is with the New Jersey Institute of Technology. There is a renewed interest in oil particle interactions due to its apparent significance in the mediation of oil spill impacts that was highlighted by reports published in 1995 by Jim Bragg (Exxon Mobil). These reports linked the recovery of oiled low-energy intertidal environments to the formation of "clay-oil flocculation" which enhanced the physical dispersion of the residual oil.

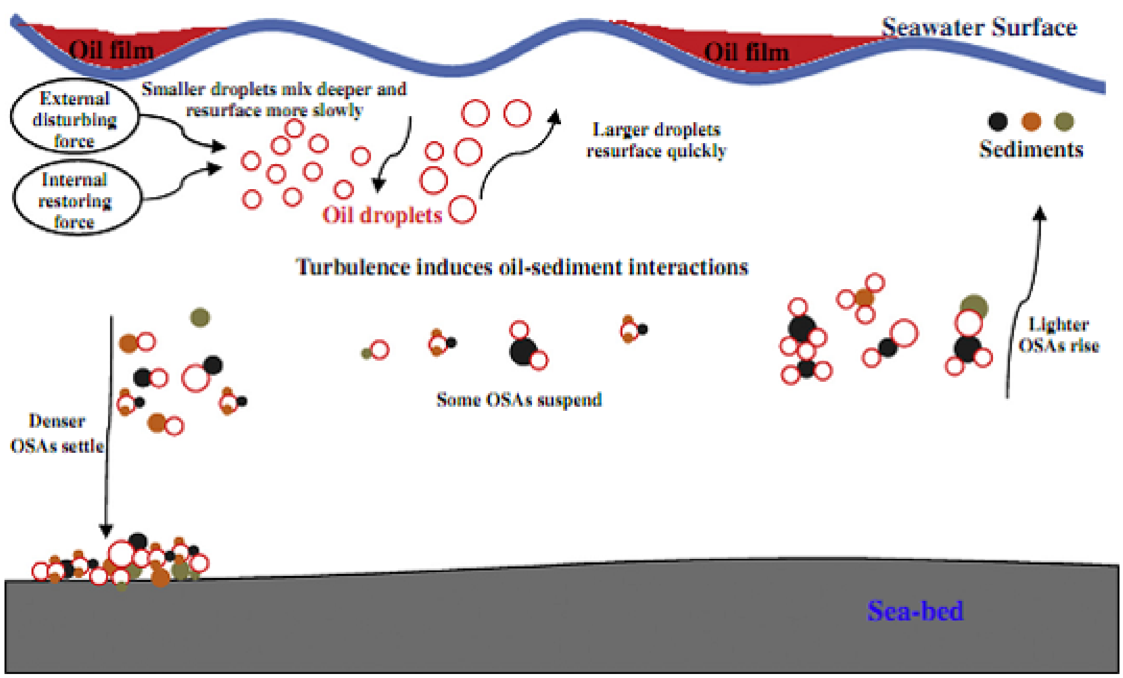

Figure 8. Formation and movement of various types of OSAs in marine systems (Gong et al. 2014)

Background: OMAs are naturally produced in high particulate estuarine and near shore waters and occur with naturally occurring suspended particles. The ingredients are suspended particles, oil droplets and energy to produce OPAs (Figure 8). The OMAs can change the fate and transport and influence the oil biodegradation rate.

Field Testing: A field test was conducted at the St. Lawrence Estuary Field Trial to evaluate the effectiveness of OMA formation as an oil spill countermeasure, to fill the gap between lab and real-world application and to gain operational experience for larger scale field trails. Detailed chemical analysis (GC/MS with hopane normalization) from these studies showed that more than 60% of the total petroleum hydrocarbon, 75–88% of total alkanes, and 55–65% total PAHs, were degraded after 56 days of incubation at 0.5°C. The alkylated PAH was degraded to a greater extent following the addition of mineral fines. This technique offers several operational advantages as a spill countermeasure for use under Arctic conditions such as reduced numbers of personnel required for its application, no need for waste disposal sites, and cost effectiveness. Questions: What are the operational conditions that support the transport of stranded oil to coastal waters via the formation of oil-mineral aggregates that can enhance natural processes to both disperse and biodegrade residual oil?

Summary of A-DROP model: a predictive model for the formation of oil particle aggregates. A predictive model for OPA formation has been developed. Through the model, it was found that the packing of particles on the oil droplet becomes denser as the suspended particle concentration increases. Confocal microscopy indicated that particles penetrate the droplet and cluster on the droplet surface.

Input Parameters: To model OPA formation we need to know information about the oil (density, viscosity, interfacial tension, size distribution, concentration), available particles (density, size and shape, hydrophobicity, concentration), concentration of anything that adsorbs at the oil-water interface (clay minerals, suspended particulate matter, bacteria, etc.) and the ambient conditions (temperature, water salinity, mixing energy).

A. Sedimentation Breakout Session Discussion Summary

The questions raised in the discussions for the modeling breakout groups highlighted that modeling MOS formation and MOSSFA events is in its infancy; although there are early models of MOS and MOSSFA formation, there are no models of the fate of MOS in the sediments. In particular, there was much discussion of what missing information would be needed to improve the predictive skills of models. For example:

- How does the presence of oil and/or dispersant affect aggregate characteristics?
- How does the presence of oil and/or dispersant affect MOS size and shape distributions?
- What environmental variables are needed to improve model predictions?
- Do we have adequate estimates of microbial degradation rates of oil?
- Are there field measurements that were not taken during *Deepwater Horizon* that could prove valuable for modeling?
- We need to be able to incorporate EPS formation and properties into the models

There was also a realization that current MOS and MOSSFA modeling efforts might not be suitable for rapid oil-spill response and tracking models and so simpler MOSSFA models need to be developed that can be incorporated into response models.

B. Prioritized Questions from Sedimentation Breakout Discussions

- How many components need to be included in a MOSSFA model
    - EPS formation
    - EPS properties
    - Use of flux data
    - Degradation
    - MOS formation @ depth
    - Horizontal transport
    - Fractal shape
    - Burn residue
    - Small bacterial aggregations.
    - Droplet/mos formation
    - Environmental conditions

- Components/composition/biophysical/parameters and interactions ?
- 2 shapes/fractal
- Oil/MOS degradation photo degradation
- Catalog knowledge ahead of time. What parameters do we need to know ahead of time for modeling – almost like a sensitivity analysis of what's going into the models, and can we measure it.
- Where is MOSSFA event likely to occur (seasonality, temperature, etc.). For example – Mobile Bay
- Need to develop simple models to include in response models?
- Modeling ecological impacts of MOSSFA/OMA → Combining MOSSFA and OMA models.

IV. SESSION 4: MOSSFA CONSEQUENCES FOR RESPONSE, RESTORATION AND POLICY (DR. DAVID HOLLANDER, CHAIR)

Dr. Nancy Kinner provided an overview on MOSSFA's impact on the post DWH response. Dr. Kinner is from the UNH Center for Spills in the Environment.

Dr. Kinner identified the different phases of an oil spill, focusing on the distinction between the different temporal scales of the response effort. The first phase, identified as the "Emergency Response" phase can include the initial operations component, the response to public health that can include fisheries closures, and the need for supplying scientific support to NOAA's Office of Response and Restoration (Figure 9).

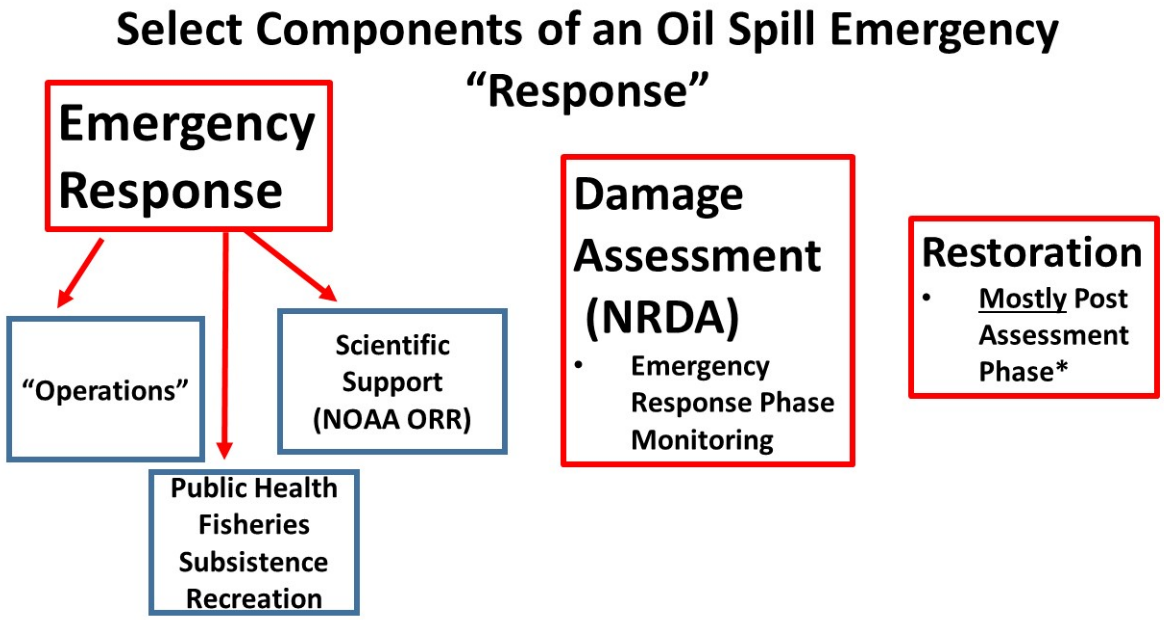

Figure 9. Schematic of the oil spill response components.

Overview of Response: The Operations piece includes the Recovery and Protection, Emergency Response, Air Operations and Wildlife Branches that are the first teams in place during a spill. The primary duties of these teams are to physically respond to the incident. The scientific support piece of the emergency is most likely the first place where the consideration for a MOSSFA event can be incorporated. Activities of the Scientific Support include trajectory modeling and to identify resources that may be at risk to the spill. It is at this stage that a model that includes MOSSFA events can be used as well as a metric for predicting any risk posed to the benthic habitat. Since 2010, there have been many meeting and workshops designed to provide a framework for the academic and industry researchers to work together and exchange information during the scientific support stage. The academic community can also be used to provide the NRDA process with key information.

Dr. Lisa DiPinto is with NOAA's Office of Response and Restoration. She discussed how MOSSFA was factored into the DWH NRDA with possible considerations for future responses.

Overview of the NRDA: The Natural Resource Damage Assessment (NRDA) is a structured legal process defined in regulations through OPA, CERCLA, CWA, NMSA, other State and Federal Acts. The process determines the amount and type of injury to natural resources and lost services from the time of incident through recovery of resources.
Resource: NRDA Trustees must document: Release-Pathway-Exposure-Injury-Restoration
https://darrp.noaa.gov/sites/default/files/Injury%20assessment.pdf

Part of the assessment is the development and oversight of an implementation of restoration plan(s) to compensate the public for injuries and lost services. By necessity, these NRDA efforts were grouped according to representative resource categories recognizing that these resource category groupings are all interconnected in the northern Gulf of Mexico ecosystem.

NRDA takes these interdependencies into account as part of the assessment process. However, NOAA cannot test or examine absolutely every injured bird, every sickened dolphin, or every place that oil had washed ashore. To do so would be cost prohibitive and scientifically impractical. For that reason, we evaluated a representative sampling of habitats, ecosystem processes and linkages, ecological communities, natural resources, and human services.

Role of dissolved oil deposition on seafloor: Marine snow interacted with the subsurface plume, which extended over 400 kilometers to the southwest of the wellhead, and it likely increased the oily floc footprint in the deep-sea benthos. Particulate oil was detected in the plume up to 96 miles from the well, dissolved oil was detected in the plume up to 166 miles from the well, and other indicators of the plume were observed up to 256 miles southwest of the wellhead. Photos of sediment cores taken aboard the R/V Ocean Veritas Response Cruise showed: (a) A representative pre-spill sediment core with compacted sediments and lacking floc. (b) A sediment core showing the presence of an overlying, loosely aggregated light-brown flocculent layer. Increased amounts of marine snow and rapid sinking also led to entrainment of oil by the marine snow and subsequent deposition of oil to the sea floor (Passow et al. 2012; Stout and German 2015; Stout and Passow 2015). Such results show that benthic resources were exposed to contaminated marine snow at least up to, and likely exceeding, 35 miles (57 kilometers) away from the wellhead. Of the seven known hard-bottom or "hardground" coral sites within approximately 25 kilometers of the wellhead, four experienced some degree of injury attributed to the spill. Injuries were documented to numerous small invertebrates such as worms, crustaceans, and mollusks that dwell in or on the bottom sediments (referred to generally as infauna or epifauna depending on their location either in or on the sediment) and play an important role in the deep-sea food web (Montagna et al. 2013).

What to consider in the future?

- Sampling considerations: capturing ephemeral data
- Where to sample based on MOSSFA influenced horizontal and vertical distribution patterns
- How to sample to capturing sediment surface floc (e.g., slurp guns, sediment traps) or water column marine snow event
- Toxicological considerations
- Sediment interaction (e.g., demersal versus burrowing)
- Exposure route (e.g., ingestion, smothering)
- Exposure duration (e.g., sessile, planktonic, mobile)
- Implications for 'recovery' timeframe? Resuspension? Implications for restoration actions?

Dr. Thomas Coolbaugh is with ExxonMobil and gave the industry perspective in considering MOSSFA in the framework of response.

Dr. Coolbaugh began his discussion with a defined distinction between marine snow, marine oil snow and MOSSFA.

- Marine Snow: Marine snow is a naturally formed shower of organic material falling from upper waters to the deep ocean. As plants and animals near the surface of the ocean die and decay, they fall toward the sea floor. Marine snow also includes fecal matter, sand, soot, and other inorganic dust.
- Marine Oil Snow: Marine oil snow is a special case of marine snow hypothesized to be associated with oil spills.
- MOSSFA: Recently hypothesized to explain the apparent deposition of large amounts of crude oil on seabed during the Macondo incident.

Alternative hypothesis: After the *Deepwater Horizon* spill, the Federal Interagency Solutions Group developed an oil budget that quantified the final locations of the spilled oil. The portion of the oil that was deposited to the bottom was classified in the “residual” category. In subsequent versions of the oil budget, the amount of oil in this residual category ranged from 11% to 30%. The presentation pointed out that the laboratory studies that simulate MOSSFA may not mimic real world conditions and that analytical techniques used to quantify the amount of deposited oil may ignore key processes that determine oil fate. The industry offers an alternative explanation for oil deposition: ‘Fresh’ Macondo crude oil can have neutral buoyancy if dispersed preventing it to rise rapidly to the surface. This increased dispersion likely occurred naturally by the turbulence of gas flow, enhanced by the use of SSDI. These small droplets of dispersed ‘fresh’ Macondo crude oil rapidly lost some components by dissolution and was rapidly and extensively biodegraded. The rapid biodegradation of the dispersed oil by marine microorganisms produced large amounts of ‘floc’ (bacterial biomass) that is evidence of extensive biodegradation. ‘Fresh’ crude oil was converted into a much smaller quantity of recalcitrant residues. This denser residue diffusely deposited on the seabed under the path of the subsea plume.

A. Response/Restoration Breakout Session Discussion Summary

Breakout group participants focused on how the research community can make contributions that are helpful to the response and damage assessment process. Discussions related to this were centered around being able to provide simple and clear protocols to responders on what to measure, and how to measure it, while keeping the Coast Guard’s response unfettered. A key impediment to this is the spatial scale at which a MOSSFA event can occur and the varying time scales of the deposition. Additionally, the concept of resuspension and secondary transport makes the damage assessment difficult. The smaller groups provided an opportunity for the response community to discuss that fact that most spills are mechanically recovered, and therefore, facilitating a MOSSFA event would not be something to consider.

Regions of particular concern were those associated with significant subsistence fishing communities. What impact would a MOSSFA event have in a region like Mobile Bay or Cook Inlet? Other agency groups may be quite interested in the likelihood of a MOSSFA event and they might need to be involved in further discussions.

B. Prioritized Questions from Response/Restoration Breakout Discussions

- Community needs industrial/management application for diagenesis model

- How will MOSSFA be factored into full response process? Need to consider both short and long term impacts. Can we develop a preparedness tool (perhaps model) to support the EIS to validate using assessment data?
- size of spill, type of oil, duration of spill, location of spill, environmental conditions, sensitive mapping areas.
- How do we monitor a MOSSFA event? And how does MOSSFA change the monitoring effort to support impact assessment/NRDA? (NEBA→SIMA)
- What is the impact of different response tools on MOSSFA (short and long term)
- Under what conditions does MOSSFA become significant enough to be considered by emergency responders or damage assessors?
- Field protocol? (for responders)
- Produce (or expand) protocol document that includes:
  a) what to sample, how to sample, when to sample for MOSSFA event
  b) consider who oil sampling during response
- Link data management and products (what data are available) that can provide information on where MOSSFA is mine recent literature to catalog how to measure MOSSFA → need standard *in situ* instrument, something equivalent to fluorometer. Measurements also need to occur over time to capture physiological changes over time.
- How do we predict and take into account the possibility/likelihood of MOSSFA events occurring in shallow water, coastal marine and freshwater systems? (Although these environments are geographically more confined and would experience smaller volumes of oil (shipping and pipelines vs unrestricted flow), these environments could experience disproportionate impact on valued natural and economic resources)

IMMEDIATE GOALS FOR THE MOSSFA WORKING GROUP

As a result of the MOSSFA workshop in Galveston the steering committee is proposing to author two scientific papers that can be published back-to-back in a single journal. The first paper would evaluate the current understanding of the MOSSFA phenomenon focusing on the mechanism of MOS formations and its sedimentation and the state-of-the science for modeling and prediction of MOSSFA events. The second paper will focus on how MOSSFA can inform oil spill emergency response, how it could be used to assist short and long-term environmental assessment to complement the NRDA process and how the understanding of MOSSFA events would be beneficial to environmental and biological restoration projects. The second paper would also address the potential of and the implications for MOSSFA events occurring in shallow water coastal marine and estuarine settings and freshwater (rivers and lakes) environments.

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MOSSFA
MARINE OIL SNOW SEDIMENTATION & FLOCCULENT ACCUMULATION

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November 26-28, 2018
Galveston, Texas

Bolded individuals are providing presentations at the workshop. Starred individuals are part of the Steering Committee.

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