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MOSSFA

MARINE OIL SNOW SEDIMENTATION
& FLOCCULENT ACCUMULATION

**MARINE OIL SNOW SEDIMENTATION AND FLOCCULENT
ACCUMULATION (MOSSFA) WORKSHOP**

October 22-23, 2013

Florida State University

Tallahassee, Florida

Facilitated by:

Center for Spills in the Environment

University of New Hampshire



ACKNOWLEDGEMENTS

The content for this workshop was developed by members of the Steering Committee: Dr. Jeffrey Chanton (DEEP-C and ECOGIG), Dr. Kendra Daly (C-IMAGE), Dr. David Hollander (C-IMAGE and DEEP-C) and Dr. Uta Passow (ECOGIG and steering committee chair). The workshop was funded by the Gulf of Mexico Research Initiative (GoMRI).

This workshop was facilitated by the Center for Spills in the Environment (CSE). CSE focuses on issues related to hydrocarbon spills. The Center is known for its independence and excellence in the areas of environmental engineering and marine science as they relate to spills. CSE has conducted numerous workshops bringing together researchers, practitioners and NGOs of diverse backgrounds to address issues in spill response, restoration and recovery.

List of Consortia and Organization Acronyms

ADIOS3	Automated Data Inquiry for Oil Spills
C-IMAGE	Center for Integrated Modeling and Analysis of the Gulf Ecosystem
CARTHE	Consortium for Advanced Research on Transport of Hydrocarbons in the Environment
C-MEDS	Consortium for Molecular Engineering of Dispersant Systems
CSE	Center for Spills in the Environment
DEEP-C	Deep Sea to Coast Connectivity in the Eastern Gulf of Mexico
ECOGIG	Ecosystem Impacts of Oil and Gas Inputs to the Gulf
GOM	Gulf of Mexico
GoMRI	Gulf of Mexico Research Initiative
MOSSFA	Marine Oil Snow Sedimentation and Flocculent Accumulation
NOAA	National Oceanic and Atmospheric Administration
SC	Steering Committee
USCG	United States Coast Guard

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1.0 INTRODUCTION

Research generated by numerous investigators suggests that accumulation of oil, mineral and biologically-derived solids on the seafloor occurred in association with the Deepwater Horizon (DWH) oil spill (April-July 2010), at rates far exceeding pre-spill levels. This material was most likely transported to the bottom in association with marine snow and/or oil mineral aggregates formed at the surface in the presence of oil. The MOSSFA hypothesis is that the formation of marine snow/oil aggregates and its accumulation at the seafloor is related to events associated with the oil spill, various mitigation measures (e.g., the use of dispersants and *in situ* burning), and increased sediment-laden fresh water releases from Mississippi River impoundments. If this hypothesis is correct then this phenomenon takes on an added global significance as 85% of deep-water oil exploration occurs adjacent to deltaic systems. To better understand the sequence of events and the oceanographic processes involved, three of the Gulf of Mexico Research Initiative (GoMRI) funded Centers (C-IMAGE, DEEP-C and ECOGIG), all of which have Principal Investigators involved in the various aspects of the MOSSFA question, received funding to conduct two workshops related to Marine Oil Snow Sedimentation Flocculent Accumulation (MOSSFA). The intent of the first workshop was to bring together researchers working on MOSSFA to provide a synthesis of known facts, identify data gaps and propose follow-up research to help resolve key questions and uncertainties regarding the MOSSFA hypothesis.

A Steering Committee (SC) consisting of Dr. Jeffrey Chanton (DEEP-C, ECOGIG), Dr. Kendra Daly (C-IMAGE), Dr. David Hollander (C-IMAGE, DEEP-C) and Dr. Uta Passow (ECOGIG, steering committee chair), met over a period of six months to develop the goals and agenda for the initial workshop. They identified three major areas for discussion: 1) Factors Affecting the Formation and Sinking of Oil Associated Marine Snow in the Water Column; 2) Deposition, Accumulation and Biogeochemical Fate of Oiled-Marine Snow on the Seafloor and; 3) The Impacts of Oil-Associated Marine Snow on Pelagic and Benthic Species and Communities. The SC developed and refined a series of questions to focus the discussion of these three major issues in a series of breakout sessions and enlisted the help of the Center for Spills in the Environment (CSE) at the University of New Hampshire to assist them with facilitation of the workshop. CSE focuses on issues related to hydrocarbon spills and has conducted numerous workshops bringing together researchers, practitioners and NGOs of diverse backgrounds to address issues in spill response, restoration and recovery related to the DHW spill.

The participants in the workshop were researchers and government scientists and practitioners involved in Gulf of Mexico and oil spill issues. All of the GoMRI Consortia, as well as GoMRI RFP 2 investigators, and federal agency researchers were contacted about participating in the workshop. Participants included representatives from the following Consortia: Deep-C, C-Image, ECOGIG, C-MEDs, and CARTHE, some RFP2 investigators and agency researchers.

Goals of the workshop, as defined by the Steering Committee, were to:

- **Define processes/frameworks leading to formation and sedimentation of marine snow;**
- **Understand what is known of spatial and temporal variation of each process;**
- **Delineate the manifestation of oil/snow in the sedimentary record;**

- **Determine MOSSFA effects (biological and chemical) on processes and manifestation in ecosystems;**
- **Integrate information from ongoing studies and develop new ideas and collaborations. It was hoped that this interaction would promote a comprehensive view of the factors controlling the formation and deposition of oil-associated marine snow and its accumulation as flocculent material on the seafloor, in the context of oil and gas release and dispersant application in the marine environment;**
- **Encourage the incorporation of MOSSFA-related processes and effects in the water column and sediments into numerical models in order to investigate marine ecosystem responses to the oil spill.**

2.0 PLENARY SESSION

The Plenary Session was organized to provide all participants with an understanding of what is currently known about MOSSFA. The Plenary Session consisted of four presentations:

- Overview of MOSSFA, including the introduction of the preliminary MOSSFA models for oil snow formation, flocculation and sinking, benthic processes, sediment biochemistry, and impacts to the ecosystem (Uta Passow);
- Oil Associated Marine Snow Surface Processes and Sinking (Kendra Daly);
- Deposited Oil Associated Marine Snow (Samantha Joye); and
- Ecosystem Consequences (Joel Kostka).

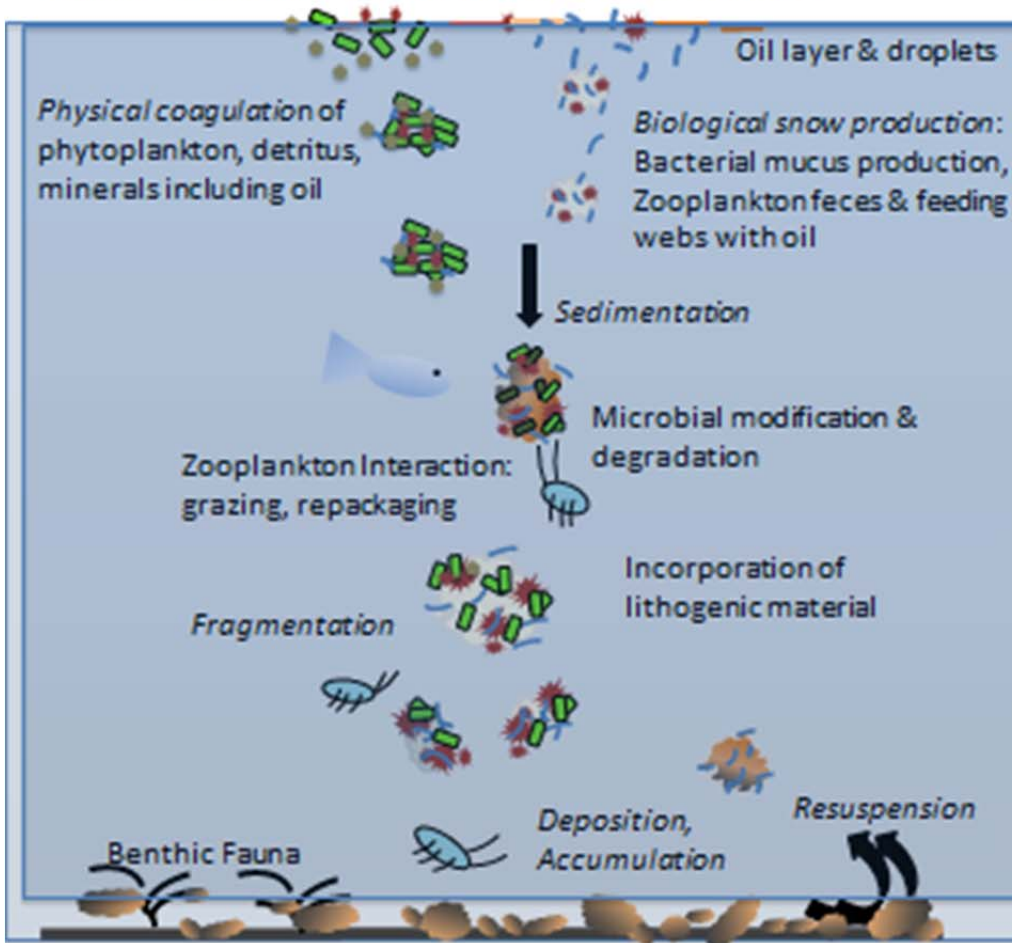
The plenary speakers drew from their own research, as well as those of other GoMRI researchers, to provide a synthesis of the current knowledge. Some of the information is currently unpublished and thus the actual presentations are not available for public dissemination as part of this report.

2.1 Overview of MOSSFA

The overall objective of the MOSSFA Workshop was to synthesize different GoMRI research results to generate a holistic, consistent picture of transport pathways of oil associated with particles and marine snow and evaluate the consequences of the oil spill and response strategies used to mediate the spill (e.g., increased freshwater diversion from the Mississippi River and diversionary channels, dispersant application, *in situ* burning, etc.). The formation of marine oil/snow aggregates is influenced by biological and chemical processes and riverine factors (Figure 2-1). Biologically-derived mucus and biopolymer production, associated with the exposure of bacteria, phytoplankton, zooplankton, feces, and molts to petrochemicals, all contribute to the formation of snow. Oil entrained into the snow and may settle through the water column. Environmental gradients also are factors. For example, river run-off from the Mississippi River and associated diversionary channels has high levels of nutrients and clay minerals and low salinity (Figure 2-2). Nutrients have an indirect effect stimulating phytoplankton growth, which leads directly to enhanced productivity and the formation of increased “marine snow”. Higher concentration of clays related to terrestrial sources result in the formation of oil-mineral-

aggregates (OMAs), the ballasting of heavier snow particles, elevated settling rates and spatial distributions. Petrogenic oil (oil derived from the earth) and pyrogenic oil (oil products resulting from *in situ* burning) may have different impacts in the formation and sinking of marine snow.

Oil contaminated marine snow: Formation mechanisms, particle dynamics, sedimentation and accumulation at the seafloor



- Formation, sedimentation and modification of oil associated rapidly sinking marine snow/ OMAs.
- Deposition, accumulation & resuspension of this material (floc) at the seafloor.
- Response of pelagic and benthic organisms and environment to such an event

Figure 2-1 Oil-Mineral Aggregate (OMAs) and Oiled-Marine Snow Formation.

Gradients: Near Major River Mouth & Radially Outward from Oil Release

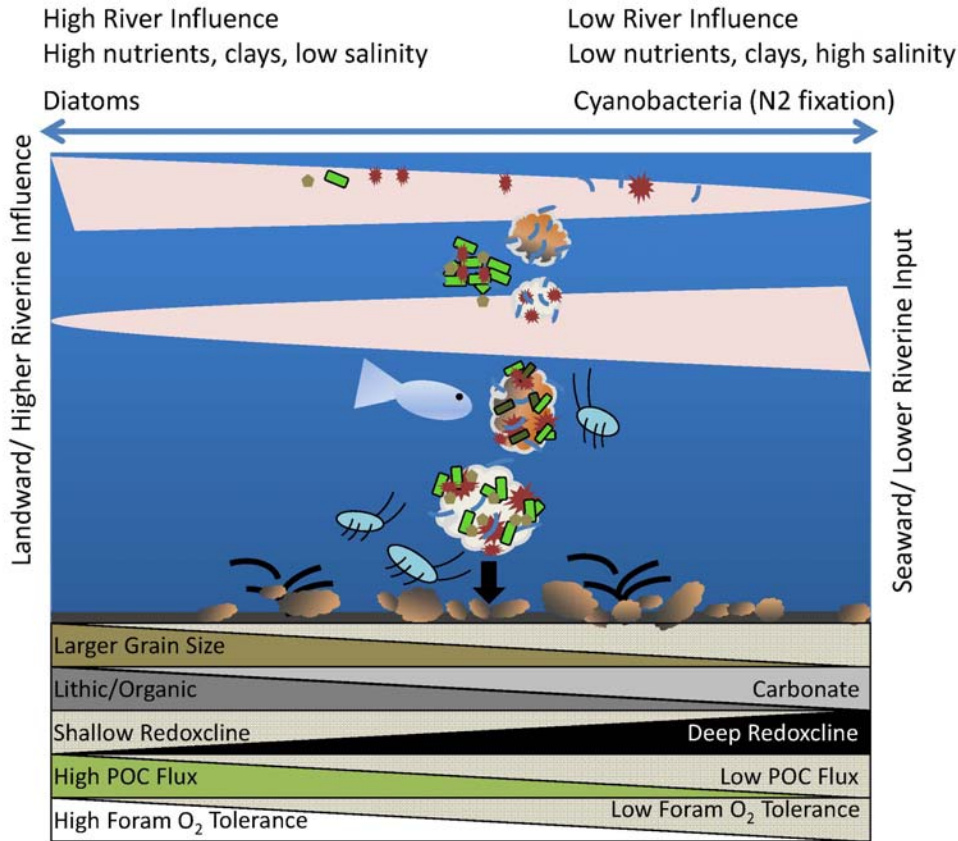


Figure 2-2 Influence of Rivers.

Lab experiments have been carried out on the formation mechanisms using different types of particles: oil snow/ microbial, marine aggregates and fecal pellets. In addition as part of recent GoMRI research, other data were collected showing:

- Very high marine snow concentrations in surface waters during August 2010;
- Oil in the water column was shown to be entering the food web as carbon;
- Sediment trap data with very high particulate organic carbon (POC) in August 2010 and decreasing thereafter;
- Rapid sedimentation to the seafloor in September 2010 evidenced by Th²³⁴ and C¹⁴.
- Very high levels of sedimentary hydrocarbons were measured at 85% of the sampling sites post DWH spill;
- High mortality of benthic foraminifera at sediment core sites;

- Data patterns in the benthic bacteria show changes in species assemblages;
- Corals were observed during October 2013 with damage to over 20% of their surface area and colonized by hydroids and they have not yet recovered.

There is an outstanding question whether mitigation strategies intensified MOSSFA processes and increased the footprint of deposition. For example, dispersants added to water decreased oil droplet size distribution, which facilitated the binding of oil with clays, algae, and bacteria; clay minerals can stabilize water-oil emulsions. In addition, algae and bacteria exposed to oil and dispersants may tend to form biopolymers. Particles resulting from the burning of oil contain pyrogenic PAHs, as well as soot particles, may have been entrained in marine snow as well.

The SC developed three preliminary models for breakout group discussion: 1) Factors Affecting the Water Column Formation and Sinking of Oil Associated Marine Snow; 2) Deposition, Accumulation, and Biogeochemical Fate of Marine Snow on the Seafloor and; 3) The Impacts of Oil-Associated Marine Snow on Pelagic and Benthic Species and Communities. The model for the formation of marine oil/snow was influenced by biological as well as riverine factors. Biologically-derived mucus (i.e. biopolymer) production, associated with bacteria, phytoplankton, zooplankton, feces, and molts etc. all contributed to the formation of snow. Oil became entrained into marine snow and began to settle through the water column. Environmental gradients also are factors: High river influence has high nutrients and clays and low salinity exacerbate the process.

Group 1: Oil-associated Marine Snow
Factors impacting the formation & modification of sinking "oil snow"

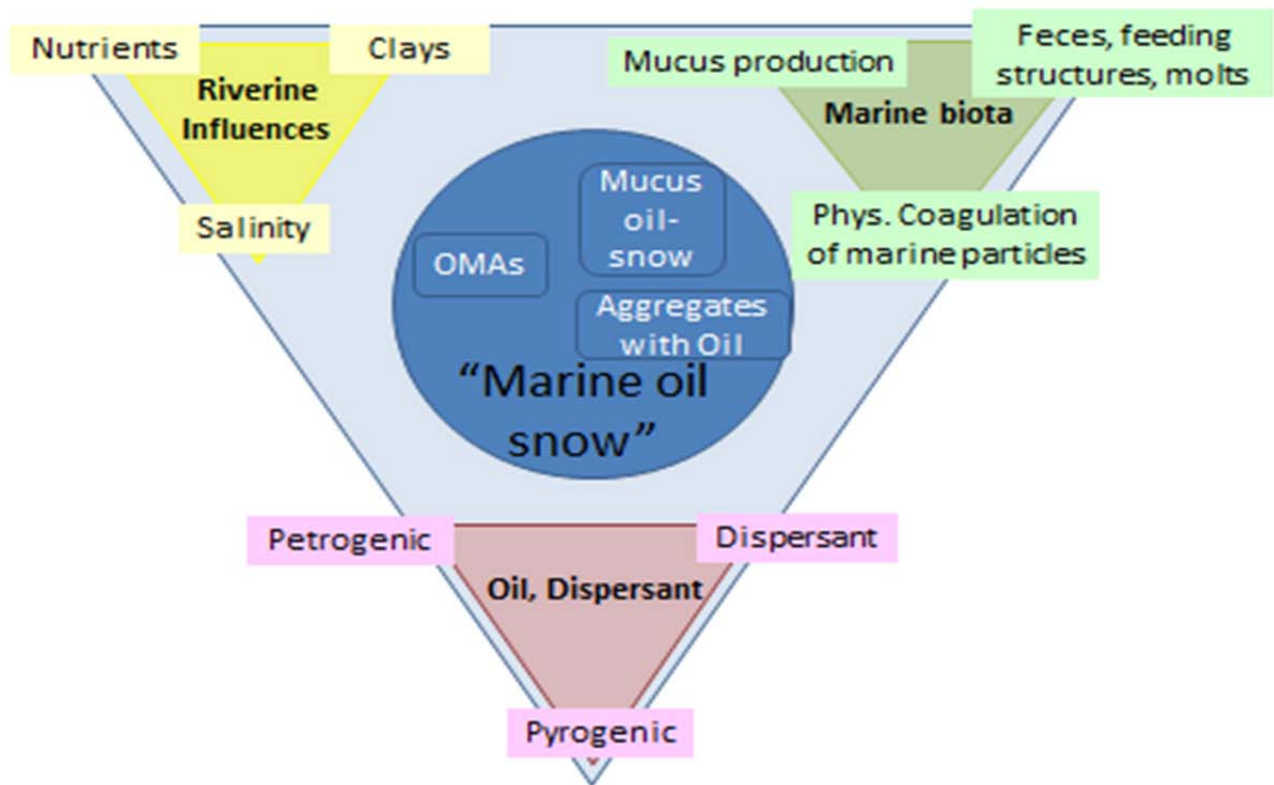
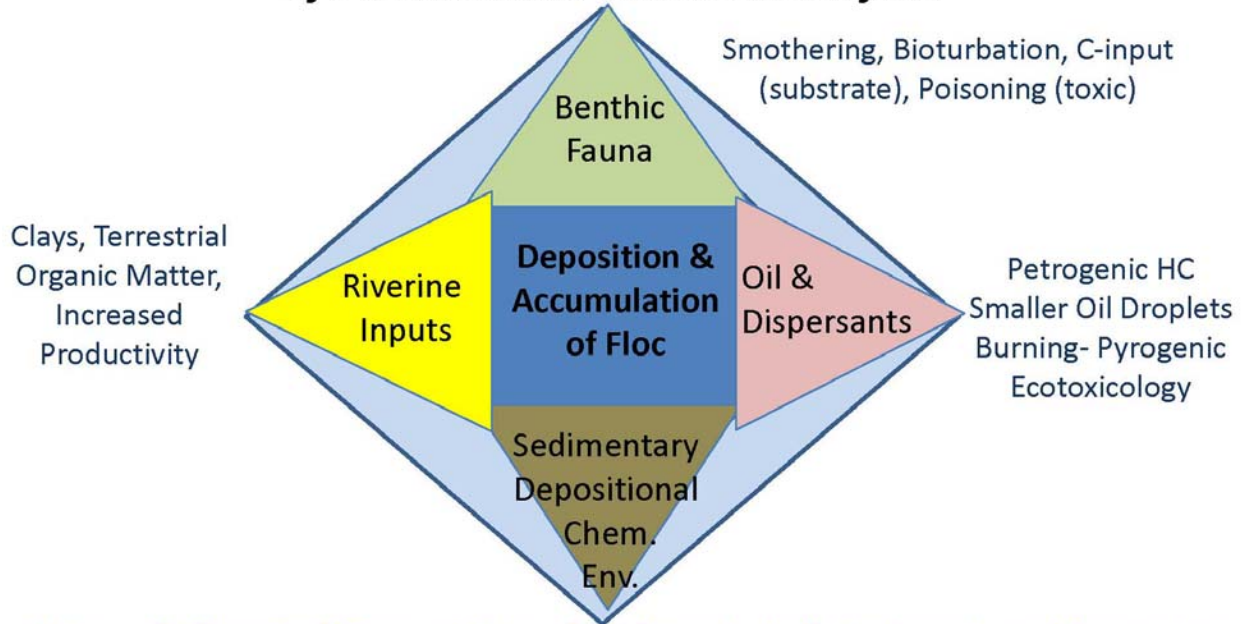


Figure 2-3 Initial Model - Factors Affecting the Formation and Modification of Oil-associated Marine Snow.

The models for deposition, accumulation and biogeochemical fate of oil and associated flocs on seafloor (Figure 2-4) was influenced by factors such as: benthic fauna (bioturbation, resuspension, feeding); oil and dispersants (petrogenic hydrocarbons, smaller oil droplets, pyrogenic material generated from *in situ* burning processes); riverine and terrestrial inputs of clays and organic matter.

Group 2: Deposition, Accumulation and Biogeochemical Fate of Oil-associated Floc at the Seafloor



Nature & Chemical Composition of Sediments Reflects Inputs and Processes

Sedimentology, Mineralogy and Chronology: Grain size, Clay Mineralogy, Radioisotope Chemistry, Sediment Resuspension, Slumping and Cross-shelf/Lateral Transport

Organic Matter Sources, Fluxes and Concentrations: Algae, Terrestrial, Microbial, Petrochemical

Redox Changes & Chemical Processes: Porewater Chemistry, Metals, Degradation Rates, Decomposition and Transformation of Petrochemicals

Figure 2-4 Initial Model- Factors Affecting the Accumulation and Fate of Oil-Associated Marine Snow on the Sea Floor

(C is carbon, HC is hydrocarbons, Chem. Env. is chemical environment).

The model for Ecosystem Impacts (i.e., those of the oil-associated snow and flocs) (Figure 2-5) were classified into: direct effects, inadvertent ingestion, and intentional uptake. Direct effects were divided into behavioral and physical coating impacts. Behavioral impacts could impact swimming or reproduction, while physical coating could be related to burial, habitat destruction or dermal uptake. Inadvertent uptake could lead to lethal or sublethal impacts to organisms. Intentional uptake, if not toxic, could lead to increased biomass production in the population. It could also result in modification of the hydrocarbons, additional mucus production and more marine snow.

Group 3: Impacts of Oil-associated Marine Snow & Floc on Pelagic and Benthic Organisms, Communities & Ecosystems

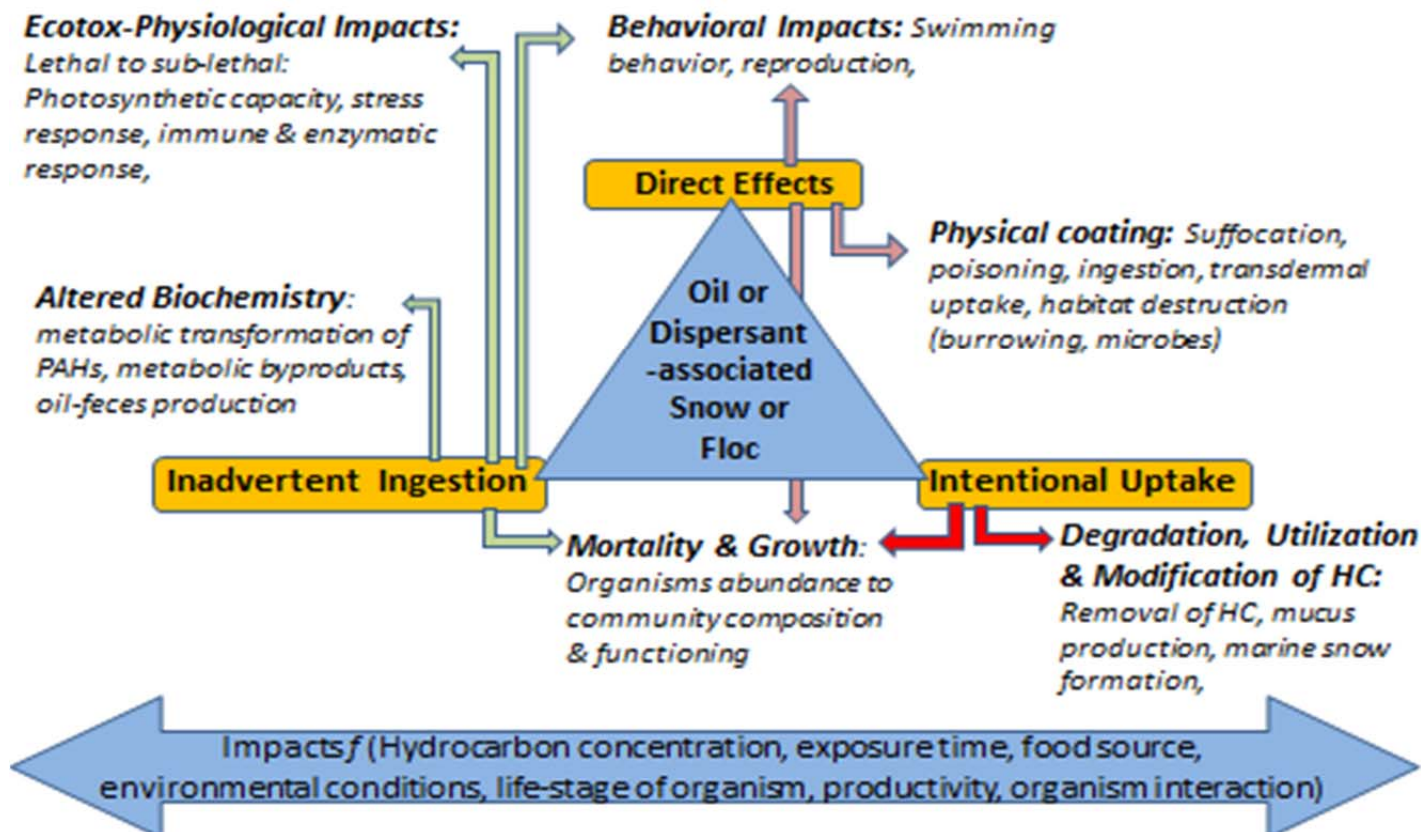


Figure 2-5 Model- Ecosystem Impacts of Marine Snow

2.2 Oil Associated Marine Snow: Processes and Pathways

Current research points to oil-associated marine snow playing a significant role in the GOM ecosystem following the DWH spill. It provided: microhabitats, food for macrofauna and fish in the water column and in the benthos, and increased settling velocity of material, including oil droplets to the bottom. There are several pathways by which oil may have been associated with marine snow particles:

- Oil mineral aggregations (OMAs);
- Physical coagulation of marine particles;
- Microbial mediated formation of marine snow;
- Formation of biopolymer by algae and bacteria “sticky” due to oil and dispersant exposure
- Doliolid fecal pellets;
- Other zooplankton ingestion, incorporation into mucous feeding webs, and fecal pellets;
- Aged or photo-chemically altered oil.

The environmental conditions during the DWH spill were unusual. Results from C-IMAGE researchers indicated that in 2010 two factors may have contributed to an unusually large amount of marine snow formation: 1) river influence - a large release over a long duration from the Mississippi River and diversionary channels creating a shallow, less dense, nutrient and sediment-rich layer offshore, and 2) the dispersed oil from the spill. MODIS satellites indicated that a phytoplankton fluorescence anomaly occurred in the northern Gulf in August 2010 as reported by Hu et al., concomitant with high chlorophyll and marine snow concentrations and high zooplankton densities. In 2013 during high river outflow but in the absence of oil, chlorophyll a was again high, while marine snow concentrations remained relatively low. It was postulated that the lack of a concurrent river influence and the oil spill was the reason for the lack of the anomaly. Sediment trap data from 2010, two miles southwest of the DWH well location, showed exceptionally high POC sedimentation (relative to normal amounts); and the initial sampling was almost entirely composed of *Skeletonema*, a brackish water diatom.

2.3 Deposited Oil Marine Snow

During sampling cruises in 2010 (August and December) and thereafter, oiled sedimentary material was observed on the GOM seafloor. Vertical mechanisms contributing to observed distributions included:

- Bio-emulsification;
- Oil-mineral aggregate formation and ballasting;
- Dispersant application;
- Soot formation from in situ burning.

Evidence of accumulation of oil /marine snow in 2010 was observed in sediment cores and by other important physical and biological measures. For example, Thorium ²³⁴ (22-day half-life) data showed a significant amount of sediment was deposited following the spill, a sediment pulse event. Natural abundance radiocarbon analysis indicated the deposition of a cm of oiled material. High polycyclic aromatic hydrocarbons (PAH) and total petroleum hydrocarbons (TPH) deposition was also found, but because of oil weathering and multiple organic matter source contributions, it was not possible to

fingerprint the oil using traditional biomarker techniques and attribute it specifically to the DWH spill. In the near-field, ~3 kilometers from the blowout site, evidence of barium from drilling muds, at concentrations exceeding background, was also found in the sediments following the spill. Pyrogenic signatures of elemental carbon and pyrogenic PAHs from *in situ* burning activity were also observed. However, the exact amount is still not known. Microbial activity (based on sulfate reduction) was observed in sediments and in the oily layer. Reduced benthic activity was recorded in samples along with an observed decline of the health of some benthic species. The length of the recovery time from these effects is still unknown in areas of heavy sedimentation. Continued long-term monitoring will be required to document the changes in community structure and timing of the recovery process.

2.4 Ecosystem Consequences

Effects from the DWH spill and ecosystem response have been observed in both the water column and in the benthic ecosystems. However, not much information was available to the speaker on near-shore environments, as most of their sampling efforts were in deep water. There are two primary sources of impact that have been attributed to the DWH blowout: the flocculent marine snow “blizzard” that was the focus of this workshop, and the oil-associated “bathtub ring”- subsurface plume that impinged on slope sediments.

Studies of impacts in the water column using radiocarbon isotopes showed that hydrocarbons entered the offshore planktonic food web. Both small suspended particles and “mesozooplankton” showed evidence of oil-derived carbon. The microbial ecology of hydrocarbon degradation involved the whole food web, including the microbes that do not specifically degrade oil. In the water column, there was a shift in microbial community structure and diversity, as well as a shift in succession of the species assemblages correlated with the presence of high levels of hydrocarbons. Among the observed taxa only those of the Gammaproteobacteria were enriched. Effects on oil-degrading and oil-assimilating microbes from deep water showed evidence in only a few species of bacteria: increases in *Oceanospirillaceae* were linked to degradation of alkanes and cycloalkanes and other taxa were linked to aromatics.

Evidence of Th²³⁴ deposition and elevated sedimentation and mass accumulation rates continued after spill and through 2013. Although Th²³⁴ calculated sedimentation rates have declined since 2010, 2013 sedimentation rates are still significantly elevated relative to pre-spill rates. Studies of foraminifera showed declines in late 2010 and early 2011. Recovery of foraminifera populations has been site specific, with observed impacts ranging from no recovery to recovery to a different community structure. Studies of benthic microbes also showed changes in community structure within a few kilometers of the wellhead. However, these data are based on only a single study.

A study of the benthic macro-fauna near the wellhead found reductions in abundance and diversity out to a distance of three km. Beyond that, moderate impacts were observed out to as far as 17 km to the southwest and 8.5 km to the northeast of the wellhead. These impacts correlated to the observed elevated TPH, PAH, and barium concentrations and the distance to wellhead. In Desoto Canyon, changes in

macrobenthic density, community structure and trophic structure were observed and are correlated PAH accumulation rates and/or the expansion of anoxic conditions in the sediments.

H.K. White et.al. conducted a study of the potential impact to deep water coral communities after the Deepwater Horizon spill. Of the 11 sites hosting deep-water coral communities examined 3 to 4 months after the well was capped, healthy coral communities were observed at all sites >20 km from the Macondo well, including seven sites previously visited in September 2009. At one site 11 km southwest of the Macondo well, coral colonies presented widespread signs of stress, including varying degrees of tissue loss, sclerite enlargement, excess mucous production, bleached commensal ophiuroids, and covering by brown flocculent material (floc). Analysis of petroleum biomarkers isolated from the floc provides strong evidence that this material contained oil from the Macondo well. Studies of octocorals and sea fans in the area of Pinnacle Reefs also showed coral injuries at three sites in 65-75 meters of water. The injuries showed evidence of retracted polyps, mucus secretions and overgrowth by hydroids. The impacted sites were in areas of dispersant and *in situ* burning spill response activity. The observed injuries in shallower waters are consistent with those observed at 1380 meters, which were linked to deep plumes associated with the DWH spill.

3.0 BREAKOUT SESSIONS

The breakout sessions were designed to have participants examine processes and impacts in greater detail and bring together their collective knowledge to better refine the current understanding of MOSSFA. Additionally, they were used to identify questions and research objectives for the future. The breakout groups were focused on different major components of MOSSFA:

- 1) **Factors Impacting Formation and Modification of Sinking Oil-Associated Marine Snow.**
- 2) **Deposition, Accumulation and Biochemical Fate of Oil-Associated Floc at the Sea Floor.**
- 3) **Ecosystem Impacts of Oil-Associated Snow and Floc on Pelagic and Benthic Organisms, Communities and Ecosystems.**

Breakout Group membership for the first two breakout sessions was organized to provide the best expertise on each of the three topic areas, integrating researchers from different consortia and disciplines. Each breakout group was led by a Facilitator and group discussions were recorded by a Rapporteur. For the third breakout session, groups were rearranged so there could be a better exchange of ideas and information from the first two sessions.

The SC developed a series of questions to guide the breakout groups. These questions were:

- Breakout Session I
 - *Refine the SC-generated conceptual diagram for your topic area.*
- Breakout Session II
 - *What data exist regarding different aspects of your conceptual diagram?*
 - *What data are being collected?*
 - *What data need to be generated by new projects?*

- Breakout Session III
 - *What synthesis products are needed to develop a holistic picture of what happened to Marine Snow during the Deepwater Horizon?*
 - *How do these products help compare what happened to Marine Snow to historical conditions (non-spill)?*
 - *How will these products help improve future oil spill response?*

For continuity, the results of all three sessions for each Breakout Group are reported together.

3.1 Breakout Group I: Processes and Pathways (**Facilitator:** Kendra Daly, **Rapporteur:** George Jackson)

This group determined that the initial model provided by the SC was basically correct, so they used it as a starting point. Discussion among the group members resulted in some additions to the model. In the area of riverine and shelf influences, dissolved organic carbon was added as an input. In the area of biological inputs to the system, the group added photochemical reactions and the effects that they have on surface processes. This issue was originally mentioned as part of the plenary session by one of the participants.

Group 1: Oil-associated Marine Snow
Factors impacting the formation & modification of sinking "oil snow"

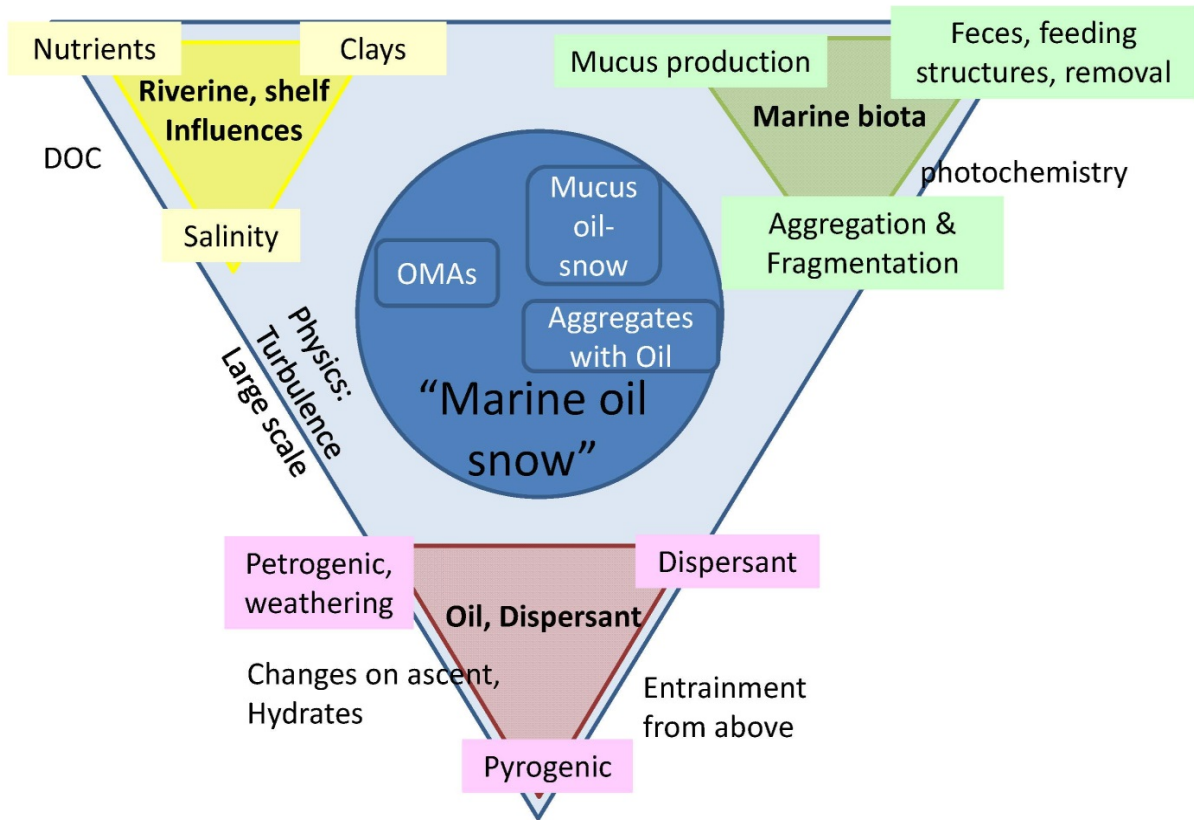


Figure 3-1 Group I Modified Model- Factors Affecting the Formation and Modification of Oil-Associated Marine Snow

The group determined there was a need to add physical processes to the model. These processes include turbulence as well as larger scale processes, such as the impact of storms on circulation and mixing. The group determined that two other processes, the effects the density of rising particles/oil droplets and their potential interaction with hydrates, need to be incorporated into the model as well.

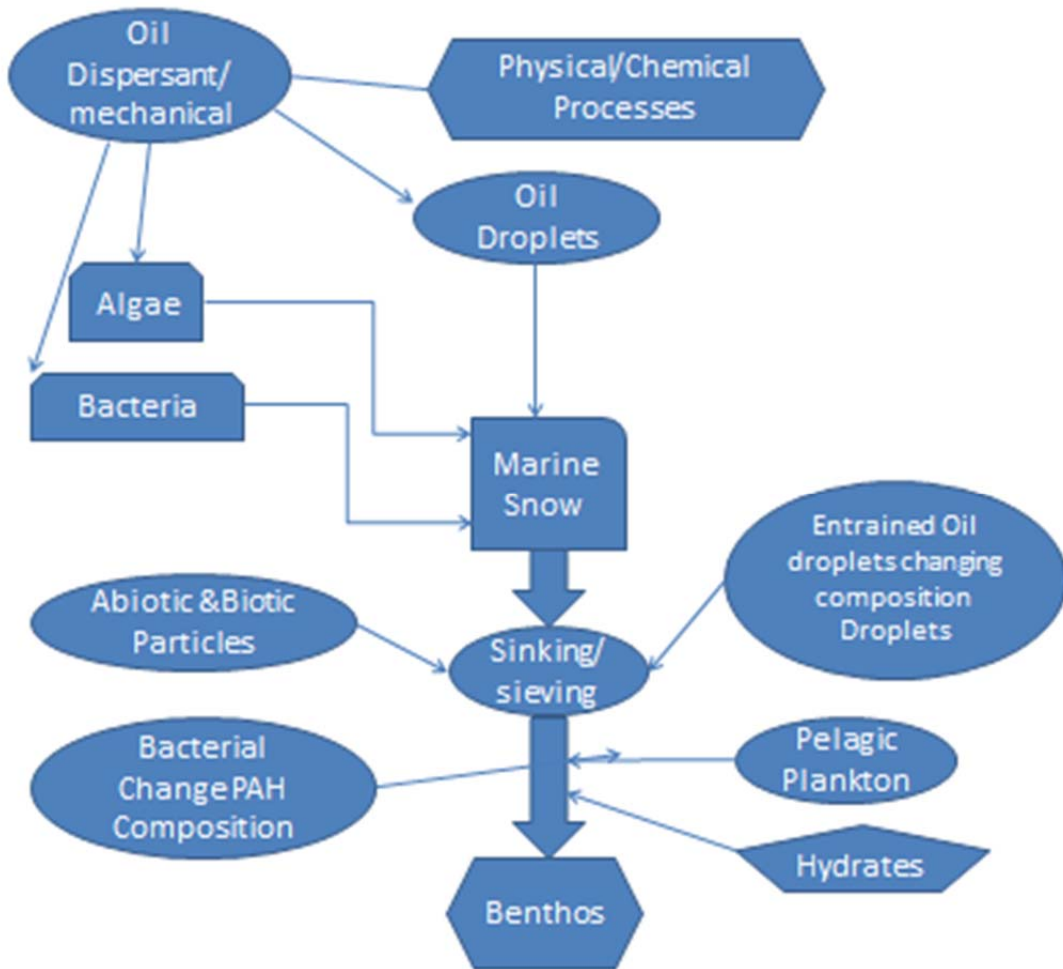


Figure 3-2 Linear Depiction of Oil/Snow Formation and Interactions as it Passes through the Water Column

The group also developed a figure that demonstrated the interaction of the processes in a linear fashion (Figure 3.2). This model will require refinement as investigators develop additional information on the interactions in the water column. The proposed pathways also provide guidance for MOSSFA researchers with new proposals that are aimed at defining the processes and ultimately enabling modeling of the formation and settling of marine oiled-snow in the environment.

The group felt that a matrix approach was also an effective way to describe and ultimately quantify factors affecting the influence of the different properties in the model. By constructing a matrix with the factors of oil dispersion, riverine influence, marine biota and physical processes across the x axis and the factors of formation, sinking, buoyancy, benthos on the y-axis, the importance of the interactions could be better defined.

Several questions were raised during the first report to all participants regarding the model. These included:

- What is the effect of different types of oil?
- What is role of Saharan dust?
- How does oil in the marine environment interact in the formation of aggregates?
- What is the role of dispersants in the process?

The group indicated that answering these questions would require more information or further study to understand their importance of the process.

During the second breakout session the group was asked to discuss the availability of data to better understand the processes and pathways of marine oil-snow formation. In attempting to answer the questions regarding available information, and the questions that still needed to be addressed, the group developed a second diagram, which attempted to better define the known inputs and interactions Figure 3-3. By using this approach, they were able to identify many of the significant research questions and data needs that are important to further defining and modeling the marine snow-oil event.

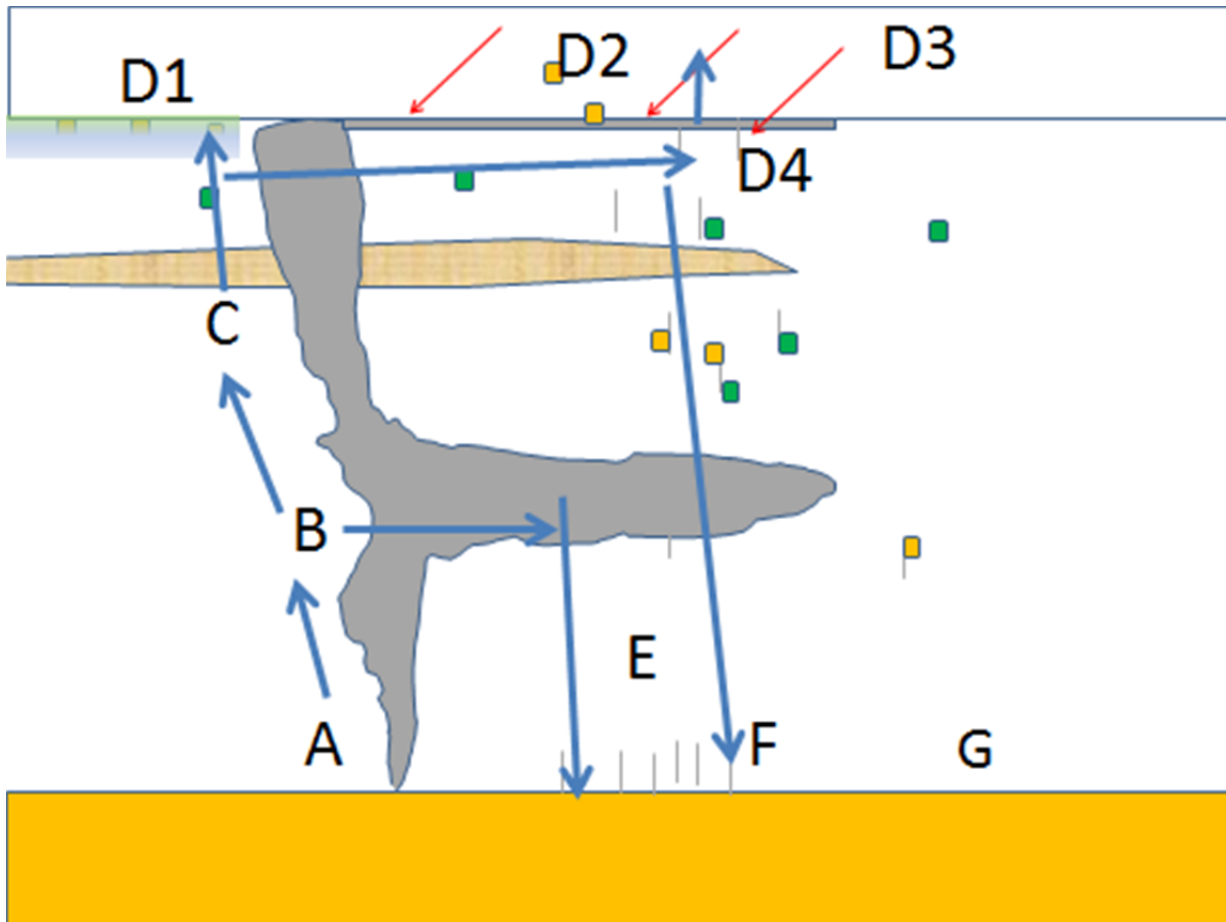


Figure 3-3 Processes Impacting Oil Droplet Size, Density and Buoyance from the Point Source to the Surface and Sedimentation to the Sea Floor.
(See key below)

- A. **Physical and Chemical Characteristics of Oil Droplets and Associated Hydrates-** What were the size distribution and density of oil droplets from a point source and how did they change over time and depth as they rise? What was the effect of dispersant addition on oil droplets at depth and did aggregation occur? What processes controlled the size and buoyancy of oil droplets?
- B. **Formation of Subsurface Oil Plume: Droplet and Bubble Size-** What processes controlled the formation of the subsurface plume? Was the plume located 1800m below the surface only present due to dispersants? What processes occurred to increase particle concentration in the plume? Did these particles sink out of the water column and end up in sediments? Did they aggregate due to the high particle concentrations? Gas to oil ratio (GOR) of droplets varied with pressure. What was the effect of pressure on methane thermodynamics and droplet buoyancy? What was the role of the internal current field on plume trajectory? How fast did the density of droplets change due to the preferential loss of lighter hydrocarbon fractions and microbial activity?
- C. **Interaction of Rising Oil Droplets with Subsurface Suspended Inorganic Particle Layers Advected off the GOM Shelf-** Water advection is generally along bathymetric contours in the

GOM, which could have acted to entrain particles, some associated with turbidity plumes from the Mississippi River. Oil Mineral Aggregates (OMAs) could have continued to rise or sink. The size of the clay particles and emulsions controlled whether the droplet/particles are buoyant or sink. Clay particles may have stabilized emulsified droplets (large body of literature). What was the role of storms in sediment resuspension? Tropical storm Bonnie (July 2010) was observed to impact current fields down to 500 m depth.

D. Near Surface Influences GOM (D1-D4) - Important Processes in the Surface Mixed Layer.

All processes impacting oil aggregate formation and sedimentation varied spatially and temporally. Increasing the density of the particles was key to forming sinking particles. What was the role of OMAs (mineral ballast) in making particles dense enough to sink? What were the spatial and temporal patterns of river outflow (nutrients, suspended clays, salinity)?

D1. Interaction of Oil Droplets with Euphotic Zone Plankton and Inorganic

Constituents Did phytoplankton and other organisms with hard surfaces interact with the oil droplets? Were species important? Did they change the properties of the droplets? Did the droplets sweep out the phytoplankton? The type and density of phytoplankton (biogenic minerals) was important to aggregate formation and sedimentation. What was the role of zooplankton (ingestion, fecal pellets, larvacean houses, etc.) in oil sedimentation? What was the impact of oil and dispersants on zooplankton behavior and survival? Dispersing the oil changed the microbial community. Did this impact mucus formation?

D2. Transformation of Oil Floating at the Ocean-Atmosphere Interface - What was the effect of UV on the oil and its density? How did evaporation of more volatile constituents change the oil? How did microbial activity change the oil? Why did experimental aggregation only occur with weathered oil? What processes impacted weathering (e.g., photochemical oxidation)? What was the role of aerosols/soot (interaction with sea surface microlayer)?

D3. New Sources of Material at the Surface - How much did dust, char, and other particles falling on the surface layer affect the oil? How did oil floating at the surface change? What changed the density of the oil, causing it to sink? How did Saharan dust input interact with the sea surface microlayer to influence OMA formation? What was the role of soot (i.e., charred combustion products of burning oil) in particle formation? How far was soot transported?

D4. Sinking of Oil-Derived Material from the Surface- What happened to the chemical and physical properties of near-surface oil when it formed the wispy sheets? What controlled the microbes associated with the near-surface oil? How/why did oil leave the surface and what were its physical properties? Physical processes also impacted aggregation and flux.

D5. Processes Impacting Aggregates During Sedimentation - What was the role of microbial activity and zooplankton (fragmentation) in transformation of sinking aggregates? How did pressure and packing of aggregates impact sinking rates? What was

the role of currents in lateral advection of sinking particles? Did oil form particles in the absence of organic-derived marine snow? How did surface-formed sinking particles interact with the subsurface oil plume?

E. Processes Affecting Sinking of Oil-Derived Particles - To what extent did particles scavenge organisms, inorganic particles and other oil droplets as they fell? Were they eaten by zooplankton and what happened to the oil and to the animals? Did incorporation of fecal pellets into aggregates increase sedimentation? How important was the presence of hydrocarbon-consuming microorganisms?

F. Processes Impacting Particles on the Seafloor- What was the recovery rate of benthic organisms after oil deposition? What were the impacts of smothering and toxicity from oil? What was the role of bioturbation? How widely was the sediment/oil distributed? What fraction of the oil settled on the bottom?

G. Processes Impacting Resuspension of Oiled Sediments - What was the role of water motion in resuspension, disaggregation and reaggregation in benthic boundary layers? What was the role of natural oil seeps? What were the relative abundance and characteristics of natural oil? Was marine snow being produced near natural seeps? How did storm-generated deep currents impact resuspended oil?

In developing this model a number of questions were immediately apparent. Aggregates formed quickly; did this process have something to do with the oil? What was the interaction of oil and particles from river input? How many of these questions could be answered if a synthesis of current data was conducted? The group identified some significant data sources. There are data on nutrients and suspended sediments from the Mississippi River, which could be used to better understand this process. River input could have several effects on the snow formation. There are also data available on the phytoplankton species present and, thus, particle size of this fraction. There are data on river outflow volume, salinity, and duration of those events that could be utilized in any of the models. Hurricane Bonnie arrived after the spill and contributed to oil sinking. After Bonnie there was much reduced surface oil. It should be determined if there is enough data to estimate the importance of the storm's impact.

Pyrogenic PAHs and soot particles derived from oil burning contributed to the formation of marine snow. Data are available on the *in situ* burning process, including the location, duration and process so that these sources could be evaluated as to relative contribution. The contribution of Saharan dust particles is currently not known; however, data on the dust concentrations are probably available from NOAA. Fresh oil did not sink; it is weathered or degraded oil that was responsible. More information needs to be collected on how Pickering emulsions work and how they contributed to the marine snow process

Questions need to be answered on the role of zooplankton in the process. Were zooplankton changing the particles as they sank? Were gelatinous zooplankton involved in the process and if so how? Information also needs to be gathered on the role of the benthos in MOSSFA. With the burial of certain benthic organisms was there a change in the bioturbation process? How did natural seeps interact with marine snow? There is a need for more baseline data for the benthic organisms as well as for zooplankton.

During the third breakout session the group identified a number of big picture questions that still need to be answered regarding marine snow and oil interactions:

- How did it affect humans?
- How is it still affecting ecosystems?
 - Did it strip nutrients?
 - Impact the bottom?
- What can we predict regarding MOSSFA and what do we need to make better predictions?
 - Size distributions of source particles,
 - Phytoplankton concentrations/primary production,
 - Surface DOC concentration,
 - TOC(POC+): microbe, phytoplankton, zooplankton,
 - Presence of genes coding for biosurfactants and emulsifying compounds,
 - Thermodynamics of biopolymer formation in presence of oil and surfactants,
 - Size and types of particles, especially inorganic particles and impact of dispersant on their surface properties,
 - Response of the benthic community to inputs of organic/oil matter,
 - Role of community composition including shelf vs. deep community differences,
 - Nutrient concentration in surface waters,
 - Coding for hydrocarbon degradation genes; do they have the ability to work with dispersants and dispersed oil,
 - What constitutes the water column biological community,
 - Oil composition and state during the process,
 - Physics: mixing and advective processes,
 - Atmospheric factors affecting MOSSFA including weather, seasonality, and UV.

The group identified a few synthesis products that would be helpful and that these data may be available:

- Times series distributions of nutrient fields in comparison to historical mean;
- What were the influences of river outflow and ocean current control on the location and persistence of low salinity surface water?
- What was the role of turbulence in forming marine snow?
- What other systems might be used as proxy sites to understanding the system (e.g., Ixtoc Campeche Spill, Taylor Energy Site)?
- Maps showing effects of snow sedimentation on the benthos;
- Maps showing the extent of spatial distribution of marine snow formation near surface;
- Maps showing impacts to coral;
- How much plankton was brought to the ocean bottom by the snow/oil interactions?

3.2 Breakout Group II Accumulation Rates and Fate (**Facilitator:** Jeff Chanton, **Rapporteur:** David Hollander)

Changes in particle density affect the settling of material. This settling is important for delivery of nutrients and clays to the sea floor. Sediment trap data showed that the lithogenic (i.e., silts and clays) component constituted 85% of the settled material. Planktonic inputs of carbonates and organic carbon and terrestrially organic matter composed the other significant portions. Comparison of different time periods indicated that even when changes in flux rates occurred, these inputs did not change in composition. Cores taken after the DWH documented the change in petrogenic to pyrogenic material in the deposited sediments. These cores also showed lateral dispersion along isobaths away from the wellhead.

This group accepted the initial diagram (Figure 2-4) as a starting point, but developed a new diagram to accompany it that attempted to be more dynamic by identifying the source, fate, and potential reentry in the water column by accumulating sediments (Figure 3-4). The new figure captured both the long term accumulations and the pulse of DWH marine snow-oil event.

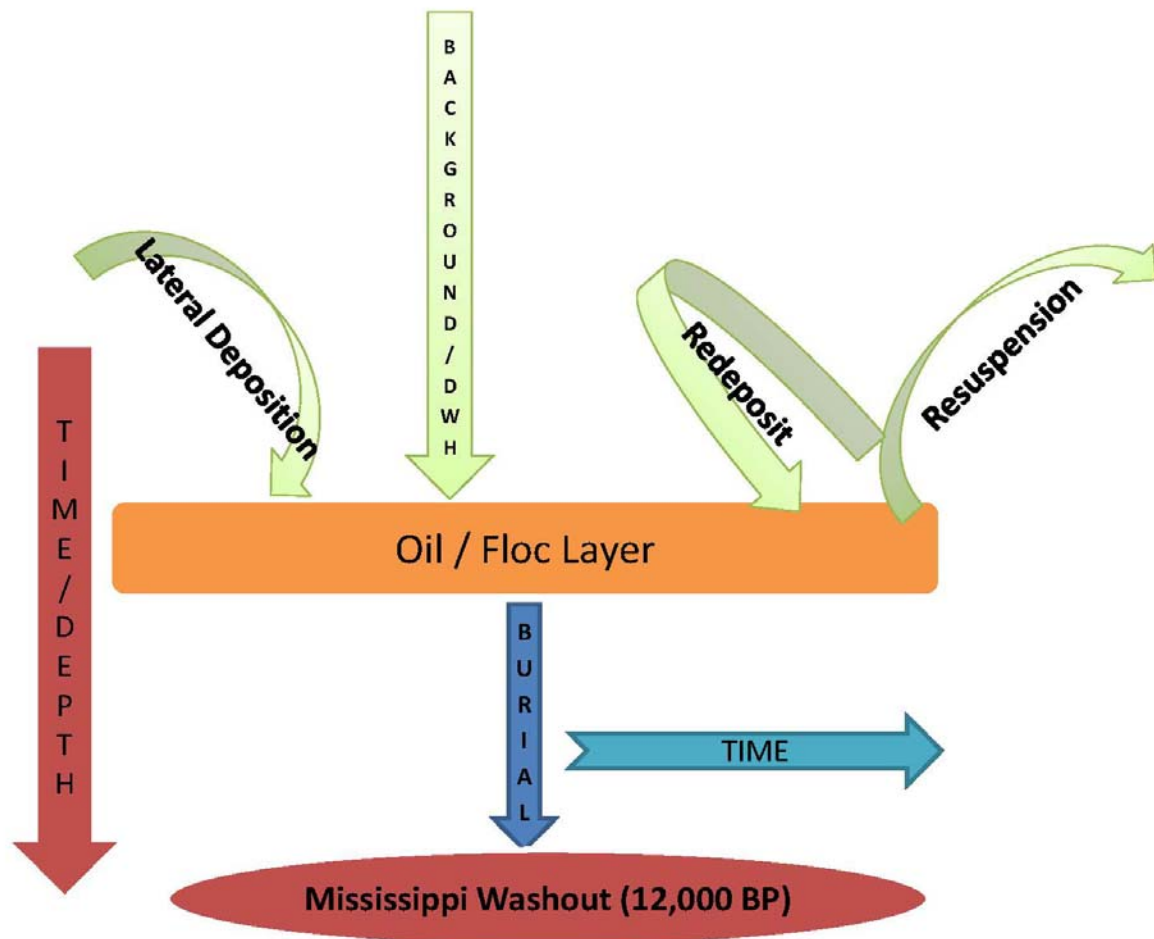


Figure 3-4 Processes Impacting Oil/Marine Snow in Bottom Waters

Figure 3-4 also illustrates the potential for lateral movement of sediments and snow as was observed by a deployed camera which imaged marine snow particles at the ECOGIG Station in the Mississippi Canyon. Other processes captured by this model (e.g., macrofauna bioturbation, resuspension, microbial processes and micro-topography) also had an impact on the marine snow-oil layer observed in the sediments.

A number of questions still remain to be answered to help develop our understanding of the factors influencing the observed floc layer in sediments.

- What happens to the floc layer over time?
- Will the observed signal in the sediments be preserved so it can be tracked over time?
- What were the relative values of the various factors that impact the movement or presentation of the marine snow-oil layer in the sediments?
- What is the importance of continued burial by natural sedimentation and microbial degradation to the reduction of future impact of oil to the benthic environment including resuspension?

There are existing data to characterize the pre-event background conditions on the outer shelf and slope. A post-event series of cores also exists at exploratory sites for 2010-2013; this time series of core data needs to be continued in order to be able to track the processes affecting the DWH related floc. Data also exists for:

- Fluxes of oil accumulation rates (petrogenic/pyrogenic) at selected sites;
- Rates of hydrocarbon decomposition, and respiration rates at hot-spots;
- Sedimentation rates, but these need broader geographic coverage;
- Profiles and distributions of sedimentation (at limited sites); and
- Ecosystem characteristics (e.g., microorganisms, macrofauna, some benthic fish).

Although there is a growing body of knowledge about the sedimentation, accumulation, and fate of the DWH marine snow-oil event, some significant data still need to be collected to better understand the fate and impacts of the oil in the benthos. In particular, there is a need to develop time scales for processes and events. There is also a need to understand different floc formation, the timing of formation and the reason for algal versus bacterial action. More data are needed on stratigraphic changes that occurred in the sediments, their nature, texture and composition as related to the marine snow event. A better understanding is needed of what controls the persistence and degradation of the hydrocarbons. In addition, it is important to understand how long the oil and oil/flocs will remain. More information is also needed on microbial communities, redox and sediment oxygen demand interactions to understand their role in the degradation of the hydrocarbons.

Information on seafloor processes and overlying sediments is needed to better understand the roles of bioturbation, bottom currents, resuspension, and benthic recovery in areas impacted by the DWH marine snow/oil event. Data on benthic-pelagic coupling related to snow are important to understand the flux of materials as identified in the model.

Finally, there is need to understand ecosystem recovery from this event, the changes that have occurred or will occur to bacterial, meiofaunal and macrofaunal communities. This will require a better understanding of natural and impacted spatial heterogeneity, as well as the factors controlling the recovery process.

The group identified the need to produce distribution maps showing the types of data being collected currently by GoMRI and other research efforts. Examples of these maps include:

- Oil coverage;
- Dispersant use and its deposition and accumulation in sediments;
- *In situ* burning sites;
- Mississippi River discharge plume;
- Benthic community data;
- Observed surface flocculation;
- Pelagic and benthic impact data.

In addition to the interactive data maps, there is a need for the development of nested numerical models. These models should include the processes of aggregation, nutrient-phytoplankton-zooplankton models (NPZ), far-field hydrodynamics with an oil module, ecosystem-scale sources and fluxes, processing

(including water transport), deposition, spatial and time functions, and impacts on various trophic levels with the development of mathematical terms for each level of the nested models. These models would be valuable for response and restoration specialists during future oil spill scenarios.

3.3 Breakout Group III Ecosystem Effects (**Facilitator:** David Hastings, **Rapporteur:** Carol Arnosti)

The group initially found that the topic of *Ecosystem Effects* was very large in that it encompassed all levels of the ecosystem (i.e., bacterial, plankton, benthos, fish, mammals, wildlife). Thus, it was determined that the initial diagram provided was inadequate because it did not address the ecosystem complexity or interaction with the geochemical cycle. As a result, the group developed a new model that attempted to address different parts of the ecosystem independently (Figure 3-5); the independent triangles could be combined to try to find points of interaction between the various parts of the complex ecosystem. This concept was developed to examine how MOSSFA affected ecosystems positively or negatively, and at different levels, (e.g., individual, population, community). This model allowed for an analysis at a “big picture level” and also helped identify where data are needed to do a more detailed analysis.

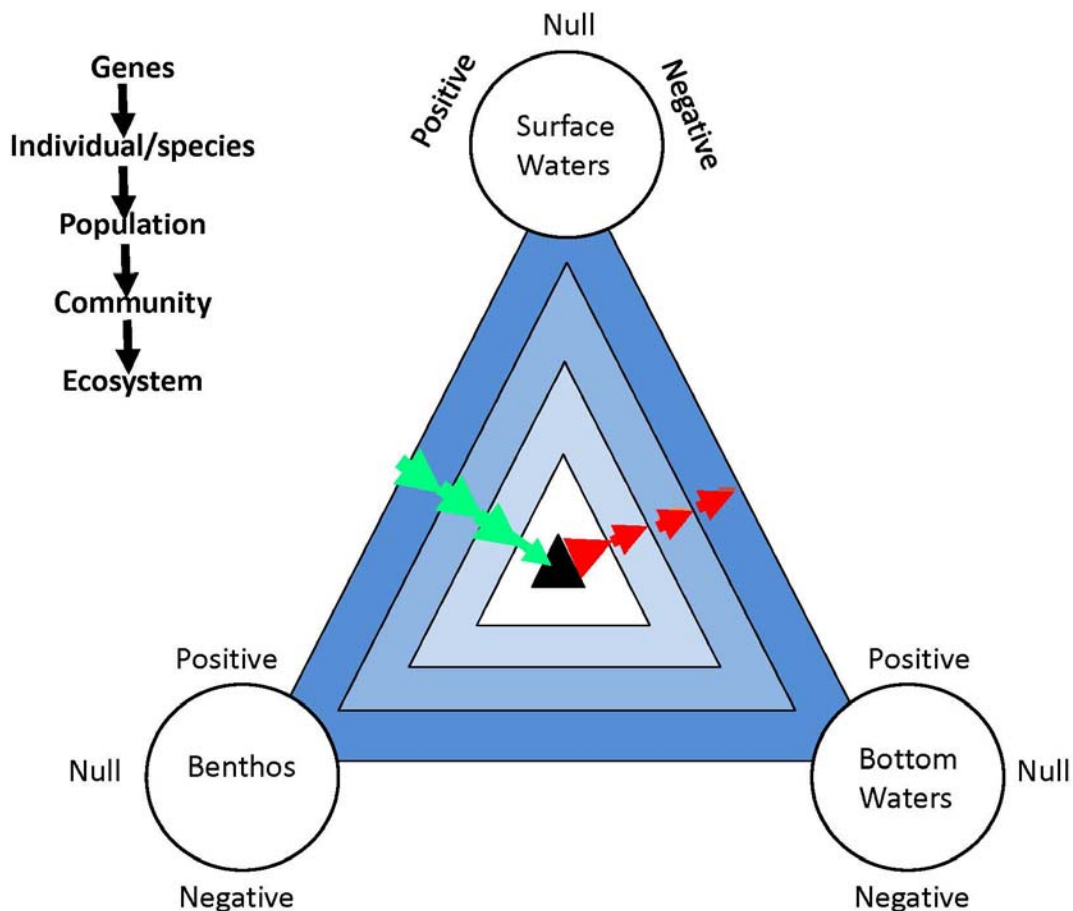


Figure 3-5 Ecosystem Effects Impact Assessment Model

For each of the triangles the conceptual model looks at the potential impacts, positive, negative or neutral, in surface waters, the benthos and mid to bottom waters. During the second breakout session, the group examined how the triangles could be used to examine impacts specifically related to marine snow-oil interactions. The “unpacking of the triangles” permitted an examination of what data might be available and what might be needed to determine impacts in various parts of the ecosystem (Figure 3-6). The group determined that the questions should be addressed at the following levels:

- Organism Level;
- Population Level;
- Community Level;
- Ecosystem Level.

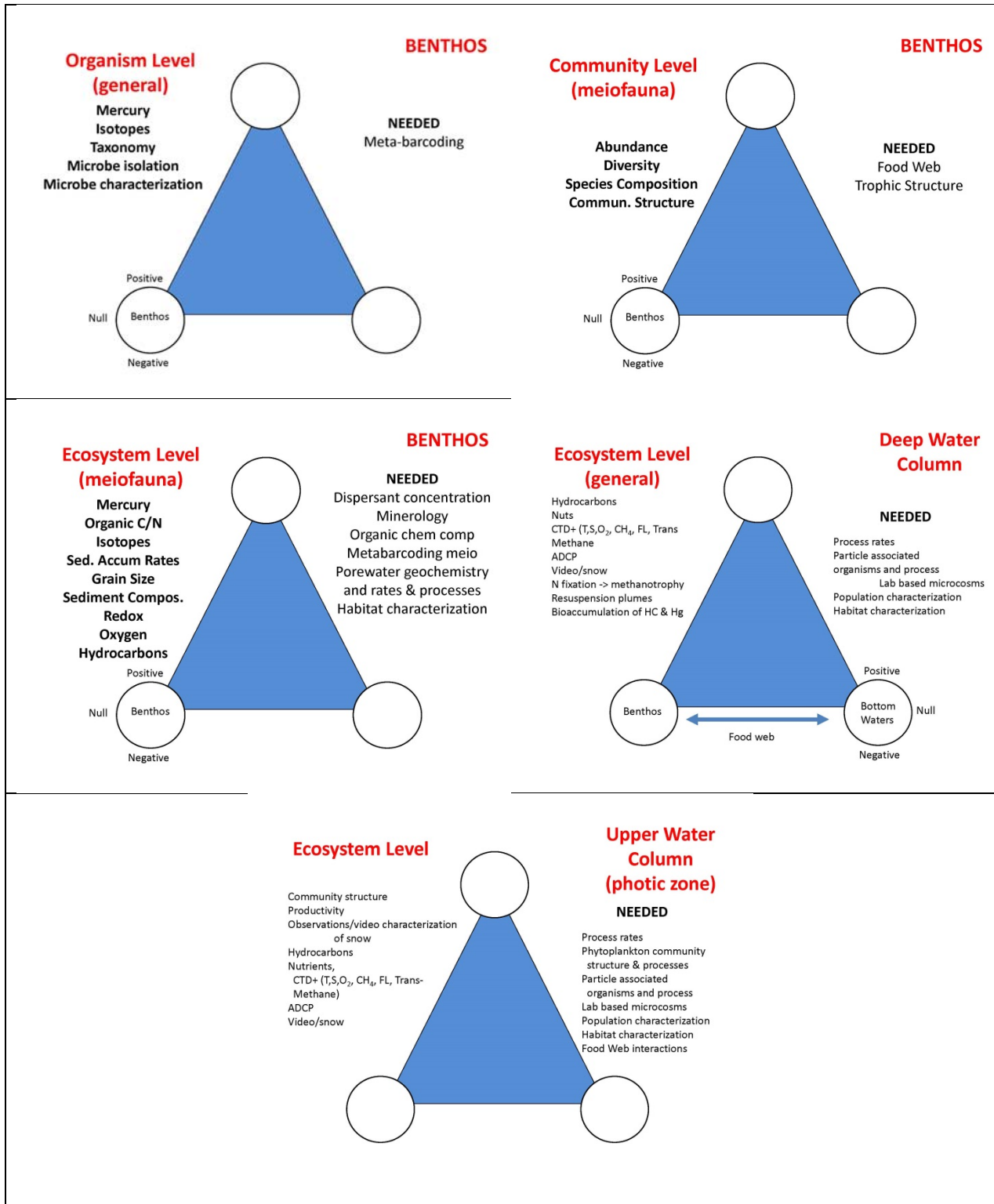


Figure 3-6 Detailed Assessment Tool Demonstrating Applicability at Different Trophic Levels

To be effective, this model would need to be applied, at least, to key species, such as those that are economically important, representative of habitats, or foundation species, at all levels in the water column and in the benthos. In order to obtain this information, laboratory mesocosm studies are needed because many of the species were not studied during the DWH spill. Laboratory studies would permit data collection on lethal and sublethal impacts. It would also permit determination of flux rates.

The group identified a number of data needs that would assist in a more effective analysis of the impacts of the MOSSFA event:

- Seafloor maps of the marine snow event (spatial extent, thickness);
- Stratigraphic framework of NE Gulf;
- Pre-spill/ post-spill comparisons for prokaryotic and eukaryotic microorganisms (community composition in water column);
- Surface water temperature, currents, salinity, wave height and wind speed and direction during the spill;
- Surface oil plume, *in situ* burning oil locations, dispersant application locations, and locations of natural seeps;
- Physical/biological data from the subsurface ocean, including sediment traps, measurements of resuspension, re-deposition, current speed, and estimates of sediment loads;
- Spatial and temporal changes in fish disease and PAH content.

The group also identified process data that would be valuable in assessing impacts and pathways related to oil/marine snow:

- Quantitative estimates of oil fate via snow (how much oil removed, how much of it ended up in the water column, in the sediments);
- The leaking Taylor Energy Site 23051 (Latitude (approximate): 28° 56.16' North Longitude (approximate): 88° 58.13' West) was identified as a great source of samples to develop a mechanistic model of oil/snow formation;
- Coupled physical/biogeochemical models;
- Coupled benthic and water column environmental data;
- Mechanistic model of snow formation examining different factors (e.g., surfaces, phytoplankton types, dispersants, oil, other variables.) to predict extent of snow formation under different conditions/environments.

There are no known studies of microbial and phytoplankton communities and marine snow formation in the Arctic. Since conditions in the Arctic are completely different, and there is a significant amount of oil drilling in the Arctic, there is a need to identify the key factors in any model of oil-floc process formation in the GOM, so the model can be modified to predict the impact of potential response actions for spills in cold climates.

The lack of some resources may limit the ability of researchers to obtain data needed to be able to better understand the impacts of marine snow-oil on the GOM ecosystem. These include: ship-time, ROV time, equipment that works in the deep benthic environment and available personnel to collect samples, analyze

data and do experiments. All of these needs require appropriate levels of funding, especially in the case of long-term monitoring efforts.

4.0 SUMMARY AND PATH FORWARD

The workshop identified a number of important issues that need to be addressed to more fully understand the processes related to MOSSFA and to develop models that could be used to predict the impacts of spill response measures on the fate, behavior, and effects of the spilled oil. The identified issues are divided into several categories: 1) Future MOSSFA Working Group/Research Collaboration; 2) Data Synthesis/Presentations; 3) Future Research Questions, and; 4) Modeling (Table 4-1).

The future research questions are numerous and complex, so the information provided here is only at a summary level and not all inclusive.

Table 4-1 Future Issues Related to MOSSFA Working Group

Category	Identified Need	Data Needed
MOSSFA Working Group	Develop a framework for studying the potential for MOSSFA occurring in other areas/water bodies in the U.S.	Develop field and laboratory protocols based on the DWH research experience
	Identify opportunities to conduct collaborative research among GoMRI-funded Consortia and researchers	Identify funding and institutional mechanisms to conduct collaborative research
	Continue activities of the MOSSFA Working Group	Identify potential funding mechanisms for the Working Group
	Expand participation in the MOSSFA Workshops especially by response professionals	Identify response professionals with GoMRI and other oil spill experience to participate
	Develop a better understanding of the oil spill response decision making process and how to relate MOSSFA research to this process	Include discussion of the decision framework as part of Working Group meetings
	Broaden areas of expertise at workshops (e.g., OMA, fish ecology, ecotoxicology, benthic ecology)	Identify researchers with interests in key areas to participate in workshops
	Data Syntheses/Presentations	Use maps of GoMRI research products to explain the impacts of MOSSFA data
	Use seafloor maps to show the extent of the marine snow event (e.g., spatial extent, thickness)	Develop interactive maps to understand potentials areas of biological impact

	Use surface maps of marine snow formation after DWH to determine the relationship to observed bottom deposition	Develop interactive maps showing the extent of snow formation on the surface
	Develop synthesis products of physical and biological factors for subsurface ocean in the GOM	Compile and analyze data from sediment traps, measurements of resuspension, re-deposition, current speed, and estimates of sediment loads
	Study pre-spill/ post-spill comparisons for prokaryotic and eukaryotic microorganisms (community composition in water column)	Compile data on water column microorganisms after DWH
	Identify the impacts to coral associated with MOSSFA	Create maps of coral impacts and merge the data with the areal extent of oil/snow
	Identify other research sites to examine for the long-term fate and recovery from oil spills and MOSSFA	Gather data on proxy sites to understanding the system (e.g. Ixtoc spill Campeche, Taylor Energy site)
	Determine the contribution of river diversion in MOSSFA development	Synthesize the data from river flows (including nutrients, sediment transport, plankton assemblages) and marine snow/oil aggregations
	Determine potential impacts and pathways to economically important (commercial and recreational) fisheries from oil/floc formation, deposition, lateral transport/resuspension and redistribution	Map available fisheries data and observed impacts
Future Research Questions	There is a need to understand different floc formations, the timing of formations and the contribution of algal vs. bacteria	Conduct research in the field and laboratory on floc formation and use models
	Develop research on MOSSFA timescales for formation, sinking, and incorporation into sediments	Evaluate existing data from field and laboratory studies to develop timescales for MOSSFA processes and develop additional laboratory studies to provide more data
	Develop research programs for tracking degradation and flux of oil marine snow in sediments	Develop a long-term monitoring programs to collect samples of marine snow/oil in sediments over time

	Develop research programs to understand restoration of benthic macrofaunal, meiofaunal and bacterial communities	Develop a long-term monitoring program to collect data on the recovery of benthic communities
	Develop research on microbial communities, redox and Sediment oxygen demand interactions to understand their role in the role in the degradation of the hydrocarbons	Conduct field and laboratory studies to study the role of microbial interactions with marine snow/oil in sediments including the role of different species and the impact of dispersants on the processes
	Conduct research on the long-term toxicity (including sublethal impacts) of oil and oil/flocs in sediments	Develop field and laboratory research on the toxicity and availability of oil and oil/flocs in sediments
	Develop a better understanding of what controls the persistence and degradation of the hydrocarbons	Conduct research on the biological and chemical factors involved in the persistence and degradation of oil/marine snow in sediments
	Determine the role of storms or major events on marine snow/oil formation	Utilize available data to determine potential impacts and important factors related to storm events
	Conduct research on the role of turbulence in formation of marine snow	How do waves and wind impact the fate of aggregates?
	What is the role of particles on the formation of the snow/oil aggregates	Synthesize data on Saharan dust and determine how marine oil interacts with dust particles in the formation of aggregates?
	Conduct research on the role of dispersants in the MOSSFA process	Conduct research on the role of dispersants including concentrations and different dispersant types in MOSSFA
	What is the impact of MOSSFA on humans, including socio-economic impacts	Conduct research on the factors important to assessing impacts to humans
Modeling	Identify the types of models that would be helpful to understand MOSSFA processes	Identify available models and the data required to model the formation, accumulation, and fate of oil-marine snow
	Determine the need for modeling MOSSFA to aid in future oil spill response	Identify models or expansion of existing models (and the data requirements) that would be helpful to responders to future spills and determine their value to practitioners

	Develop an understanding of current GoMRI modeling efforts and how they might apply to MOSSFA	Identify physical, and ecosystem modeling efforts, the scale of the models and the data requirements as they would apply to MOSSFA
	Develop ecosystem impact models for different trophic levels	Utilize the nested triangle approach to identify data required and key factors required to assess impacts
	Develop a mechanistic model of snow formation to use as a tool to predict extent of snow formation under different conditions/environments	Determine appropriate models and data requirements to understand the factors associated with marine snow formation
	Investigate the use of nested models to explain the marine snow/oil processes after deposition	Develop models nested to capture the source inputs transport, flux, particle formation, sinking rates, depositional rates, bioturbation, microbial breakdown, and time scales for the event and recovery
	Investigate how models could be used to estimate oil fate from DWH	Develop a quantitative estimate of oil fate via snow including the water column, sediments etc. Determine the type and the availability of data needed to determine the estimate
	Investigate the use of existing proxy sites to provide data for studying MOSSFA processes	Use the leaking Taylor Energy site samples to develop in the lab a mechanistic model of oil snow formation
	Develop a model for coupled benthic and water column environments	Synthesize existing field and laboratory data and supplement with additional laboratory data to develop a model to track the movement of marine snow in the GOM

4.1 Steering Committee First Workshop Summary

MOSSFA is unique in that it is a GoMRI Board funded inter-consortia working group between ECOGIG, C-Image and DEEP-C. This first and very successful MOSSFA workshop (in Tallahassee October 2013) was widely advertised and the ~50 participants represented scientists from six of the GoMRI consortia (CARTHE, C-Image, C-MEDS, Deep-C, ECOGIG, GISR), RFP2 researchers, as well as a number of experts currently not involved in GoMRI funded research. The participants included students, early career scientists, and experienced scientists.

First Workshop Highlights

1. MOSSFA and specifically this first workshop **have raised awareness in the oil spill community** that the distribution pathways of oil via their association with particles are of significance. The formation and sedimentation of rapidly sinking oil associated particles and their deposition and accumulation at the seafloor have never before been considered as a pathway for oil distribution and deposition in marine environments. It is clear that a significant fraction of the spilled oil accumulated in the sediments and that it is now susceptible to recycling and uptake via microbe, invertebrates, and upper trophic level organisms.
2. MOSSFA processes **bridge between researchers from different consortia and different research foci**: The workshop initiated the exchange of data and concepts between investigators working in different disciplines (e.g. ecologists vs. biogeochemists), habitats (pelagic vs. benthic) and using different approaches (mathematical modeling vs. field analysis vs. targeted laboratory experiments). Data integration and synthesis products were defined and first steps were taken towards these goals.
3. MOSSFA **identified important transport pathways** that affect distribution patterns of oil. Key processes and pathways that need to be considered were identified and conceptual diagrams representing these were developed.
4. MOSSFA **added a new perspective to oil spill assessment and response**, which will have to be taken into account in the future.
5. MOSSFA **established new research direction and collaborations** within the oil spill community.

To continue the momentum and engagement created by our first MOSSFA meeting, we have a poster presentation at the GoMRI Oil Spill Conference in Mobile in January 2014, where we will introduce the workshop results to the oil spill community. We are also planned a *Town Hall* MOSSFA meeting on Monday evening at this conference, to which all interested meeting participants were invited.

5.0 APPENDIX

5.1 Workshop Agenda

5.2 Workshop Participants

5.3 Workshop Breakout Groupings

5.4 Poster Session

5.5 Breakout Group Notes: Group I

5.6 Breakout Group Notes: Group II

5.7 Breakout Group Notes: Group III