Deepwater Oil & Gas Spills – Research Issues

Kalliat T Valsaraj, PhD

Department Chair and Roddey Distinguished Professor

Cain Department of Chemical Engineering

Louisiana State University, Baton Rouge, LA 70803

Tulane Engineering Forum, April 15, 2011

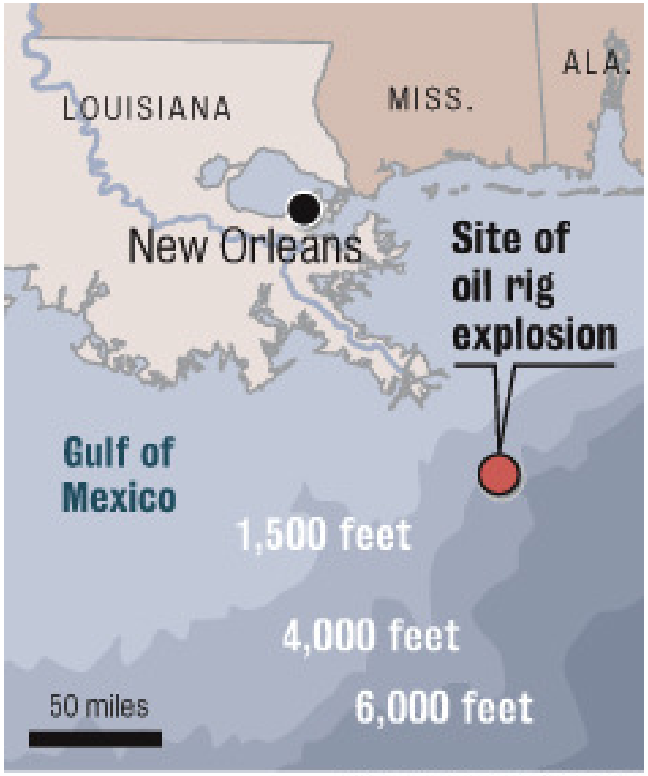
LSU

Gulf of Mexico

- Home to ≈ 24% of natural gas and ≈18% of petroleum oil (processing and production).
- Extensively developed region with high drilling activities.
- Home to a rich ecosystem with ≈ 28% of total volume of US fisheries and rich habitat for rare species.
- Mississippi river drains a third of the US into the Gulf of Mexico.

Deepwater Horizon Accident

- Natural seeps always exist in GoM.
- April 20, 2010 major rig explosion 50 miles off the coast.
- *≈1500 m below sea surface, high pressure (160 atm) and low temperature (4^{o}C).*
- Reservoir at 4000 m depth.
- 4.7-5.5 million barrels released at 53,000-62,000 bbl per day.
- Oil dispersant added at ≈1% by volume.



THE TIMES-PICAYUNE

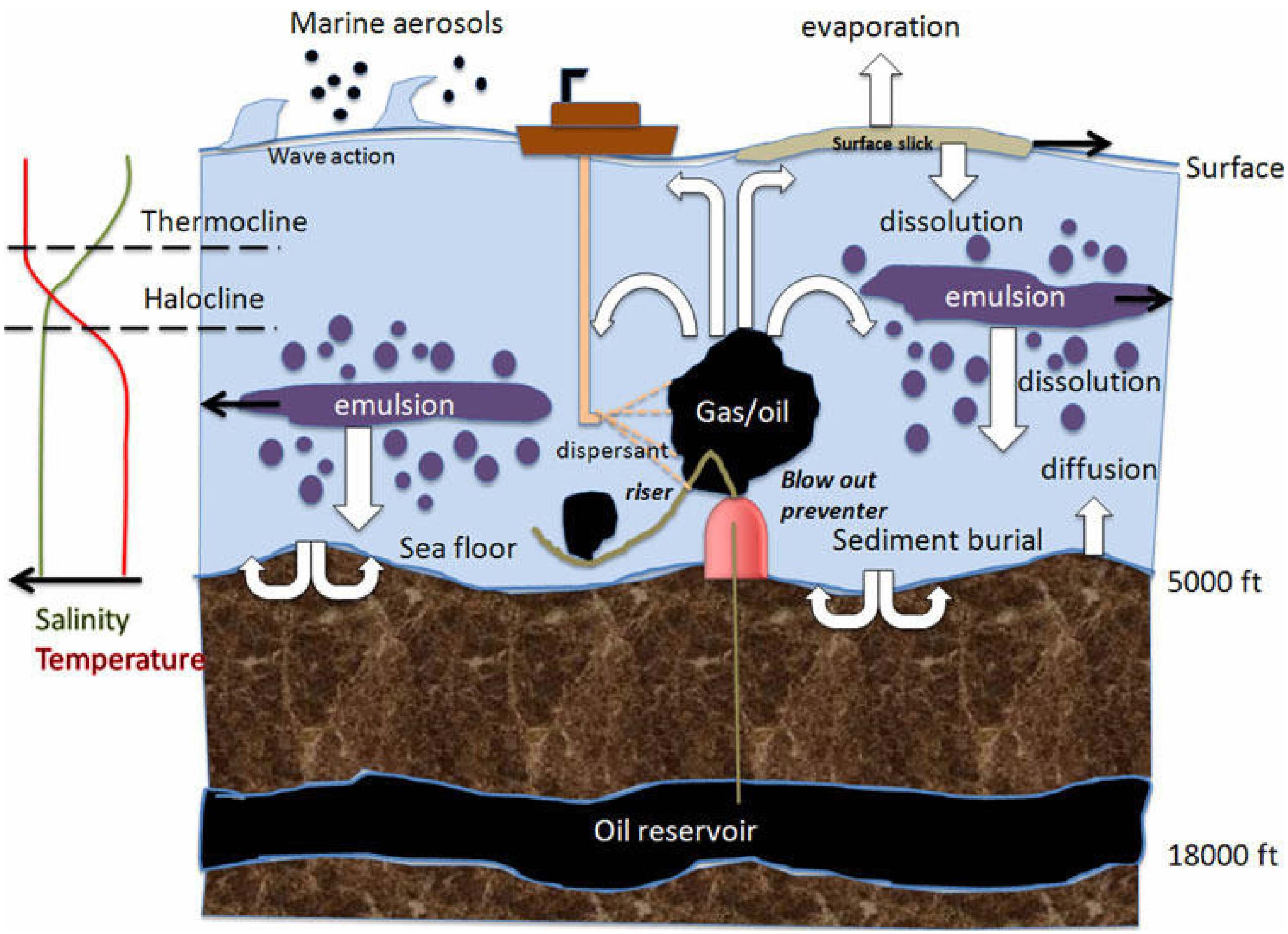
The "Big" Questions

- How much do the science/engineering community know about a massive O&G release process?
- *Where does all the material go?*
- What is its impact on the Gulf biota?
  - Should have hypothetical spill scenario analysis studying short and long-term effects, remediation and cleanup strategies.

Oil Chemical Fate and Impact Issues

- *The initiating event* – spill process, phases identification, composition (hours to days)
- *Short term fate* – spreading process, impacts and clean up (days to months)
- *Long term fate* – oil residuals, life-time persistence, chronic impacts (months to decades).

Sea Floor Leak and Oil Fate Processes



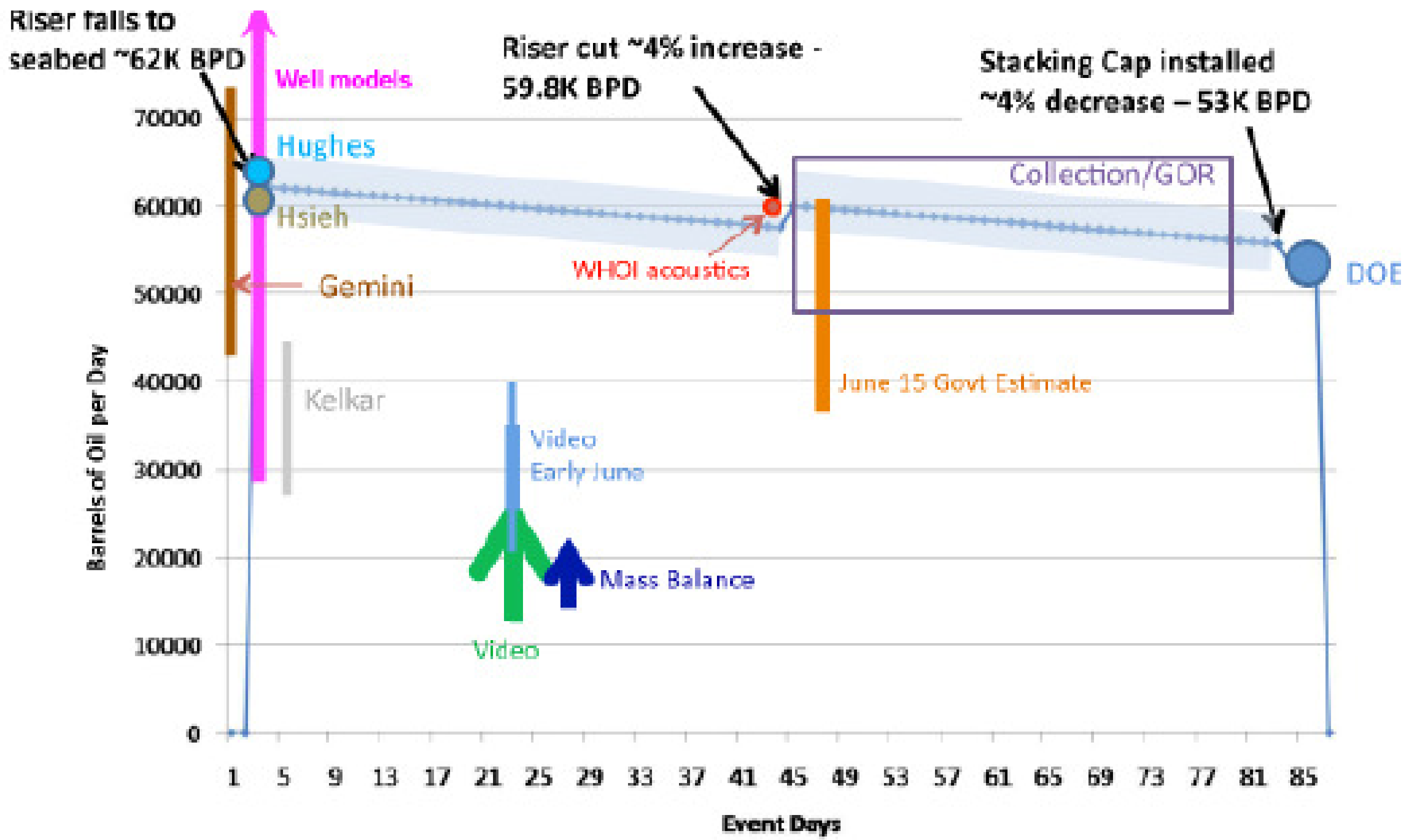
 Thibodeaux et al, 2011

The Initiating Event

- Blowout and oil phases formed – oil, liquid, solid (waxy?), and gas phase.
- Dispersions, dispersants?
- Multi-component mixture with range of chemical properties (transport and reaction) that operate on short time scales.
- Need answers to “where does it go?”

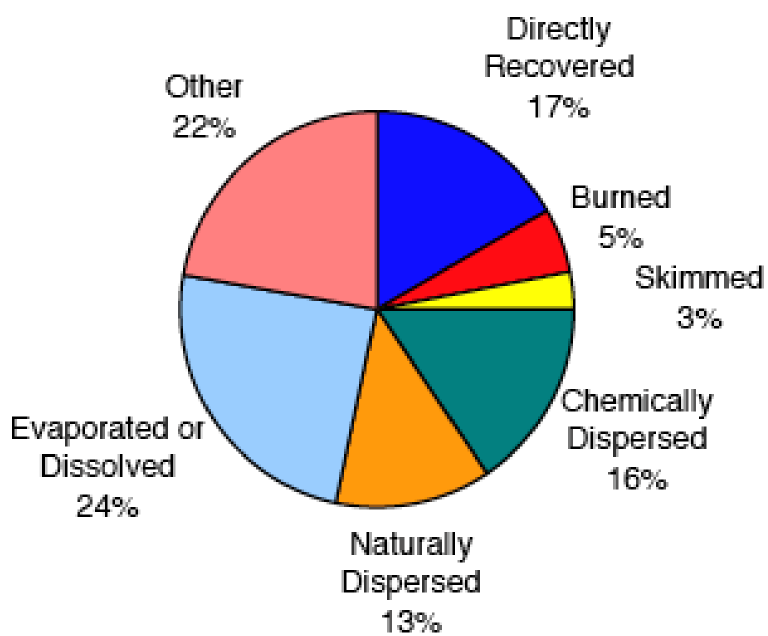
- What mass fraction remains soluble in sea water?
- What mass fraction is released to air?
- What fraction falls back to the seafloor?
- What fraction is biodegraded?
- What is the composition of the “surface slick”?
- What is the composition of the “mousse or tar-ball”?

Oil/Gas Flow Rate Estimates



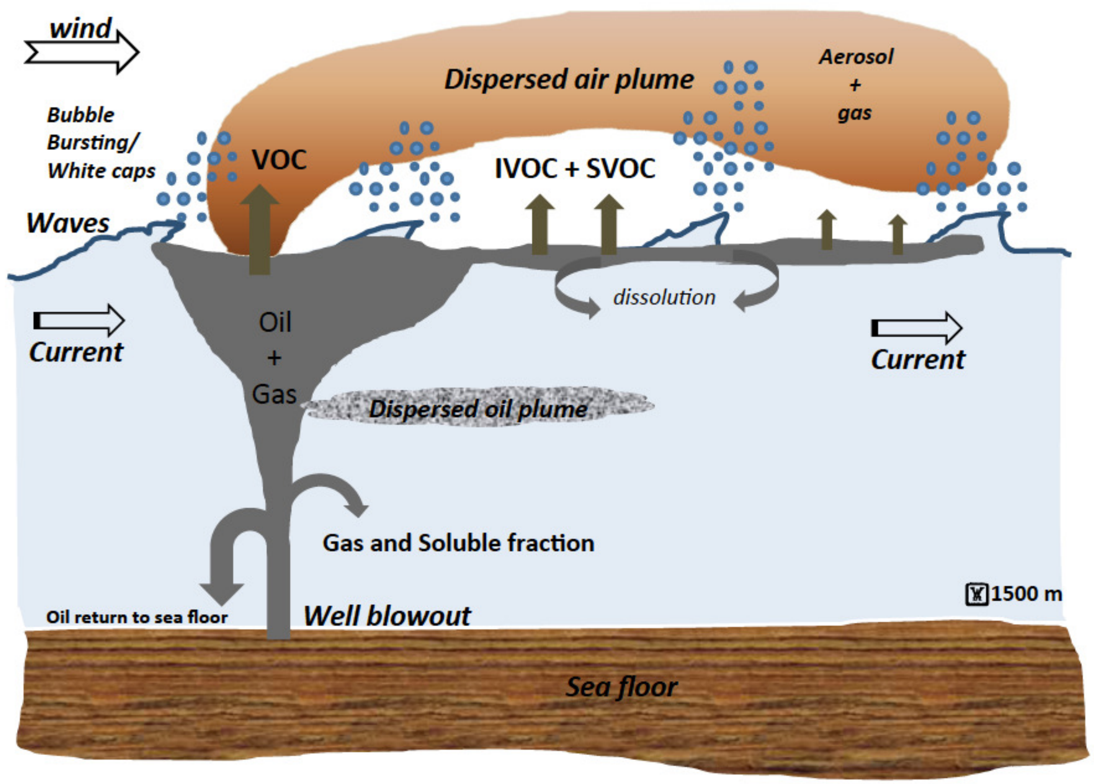
McNutt et al, 2011

Likely Fate of Oil and Gas from DWH?



Source: Reproduced by CRS using estimates provided the Federal Interagency Solutions Group, Oil Budget Calculator Science and Engineering Team, Oil Budget Calculator: Deepwater Horizon-Technical Documentation, November 2010.

Oil Fate Processes



Oil Fate in Water

- ✧Substantial plume 35 km length and 1100 km depth for months without biodegradation.
- ✧Monoaromatic input 5500 kg/day
- ✧Microbial respiration rate < 1 µM O_2 per day.

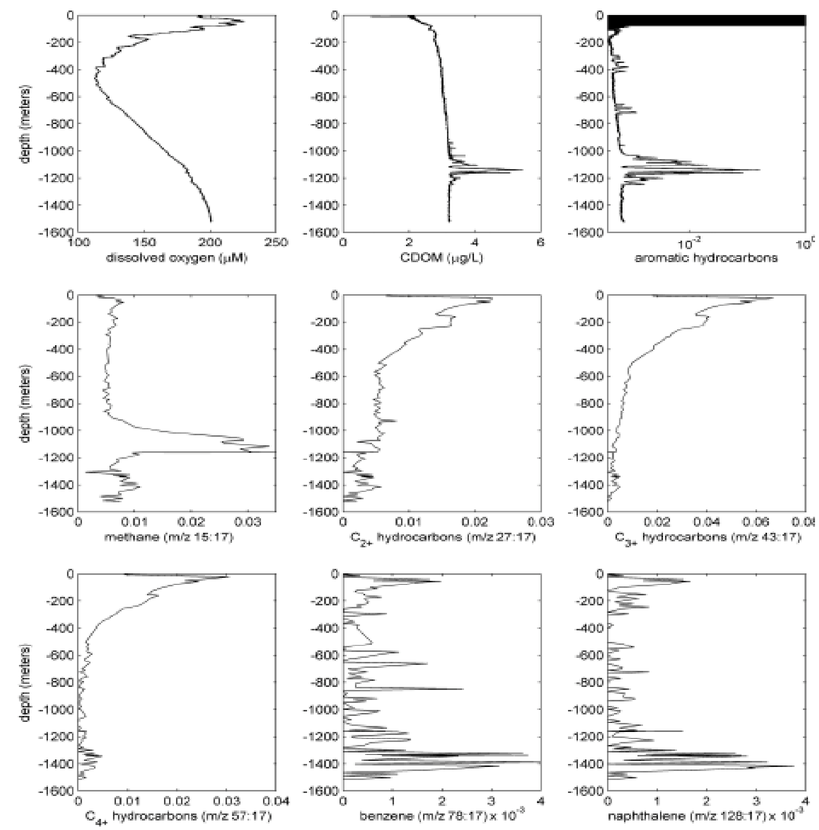
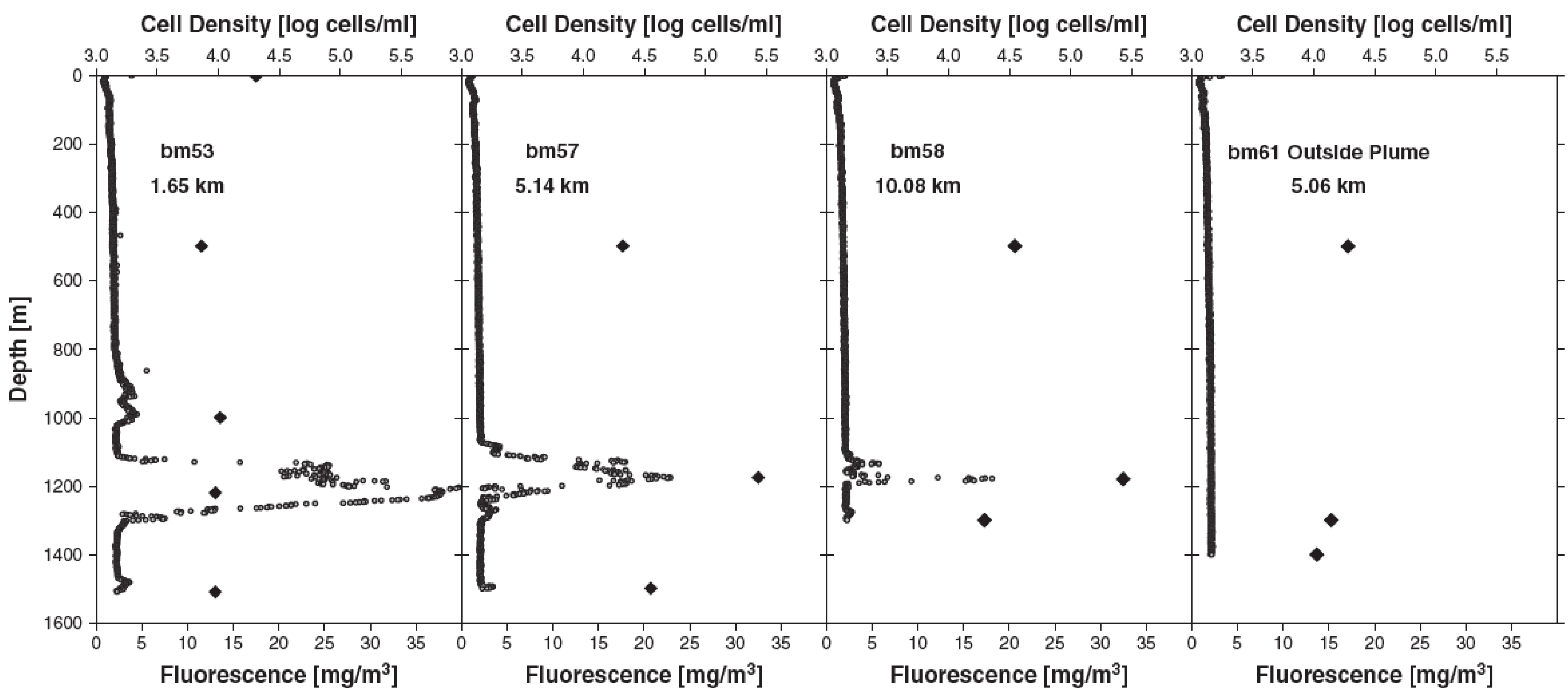


Fig. 1. Vertical profile of water-column chemistry, ~4 km from the well site at 28.7352°N 88.3892°W. Aromatic hydrocarbon values are expressed on a relative (logarithmic) scale using in situ ultraviolet flourometry, whereas hydrocarbon measurements determined via mass spectrometry are ratioed to water (*m/z* 17) to correct for variability in instrumental response. Mass spectrometer concentration values are unitless (expressed on a relative scale).

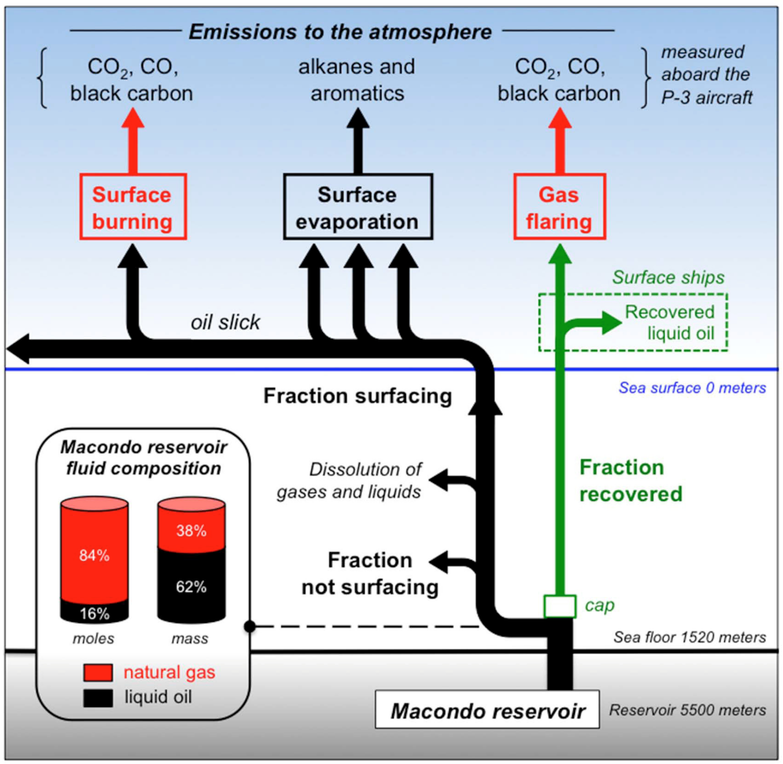
Camilli et al, 2010

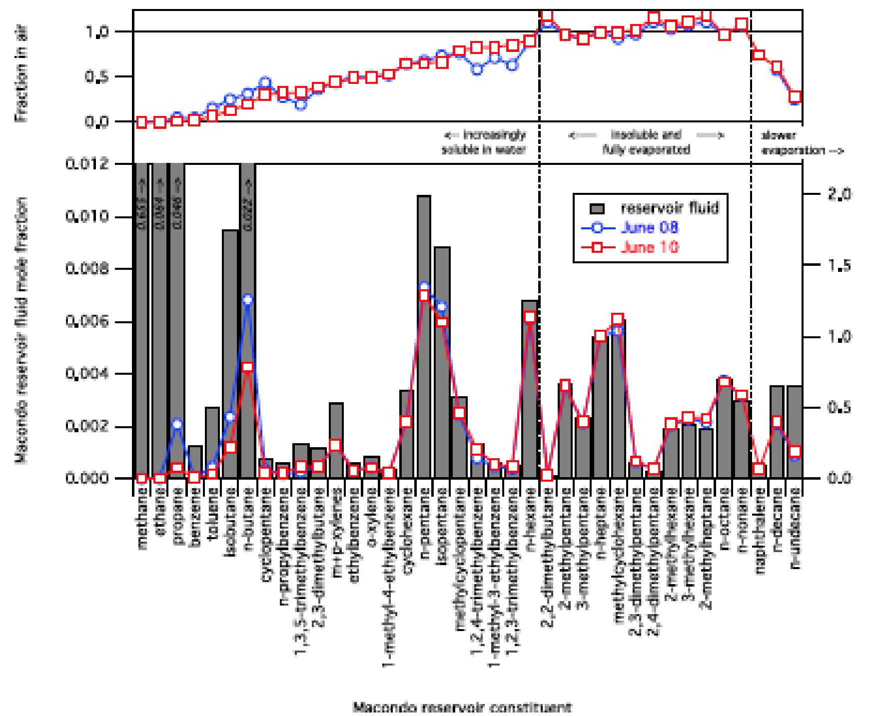
Oil Fate in Water - Microbial Activation



Hazen et al, 2010

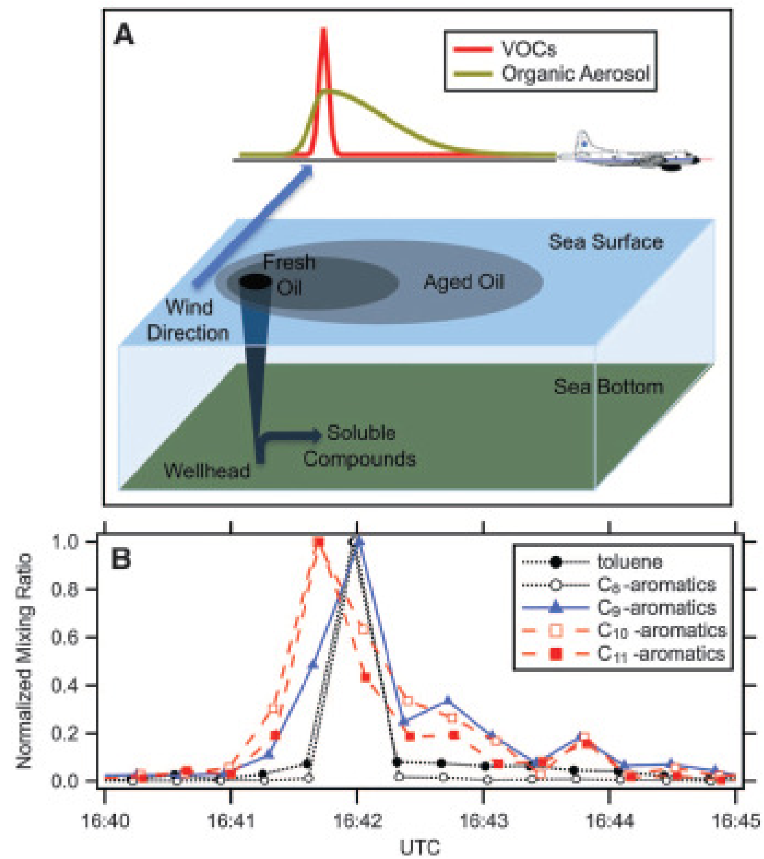
Oil Fate in the Atmosphere





Oil Fate in the Atmosphere

- Narrow plume of HC downwind attributed to evaporation of fresh oil ≈ 2×10^5 kg/day.
- A wider plume attributed to SOA from less volatile HC≈8×10^4 kg/day.

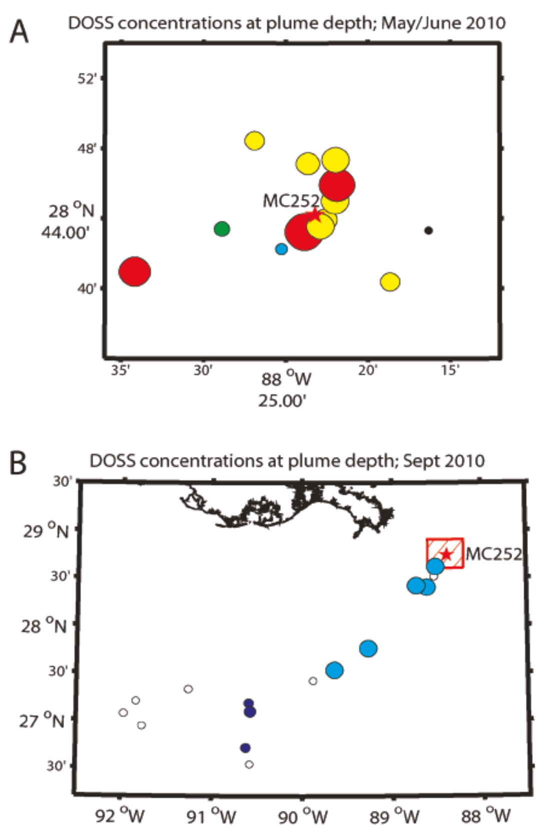


De Gouw et al, 2011

Dispersant Use in DWH Incident

- Dispersant addition:
  - Sufficient dosage of application to form droplets
  - Early application before light components evaporate
  - Lower oil-water interfacial tension to allow droplets formation and facilitate biodegradation.
- Commonly used commercialized as Corexit class.
- Little known about efficacy at high P and low T conditions – sub-surface application.
- How do gas hydrates effect dispersant addition?

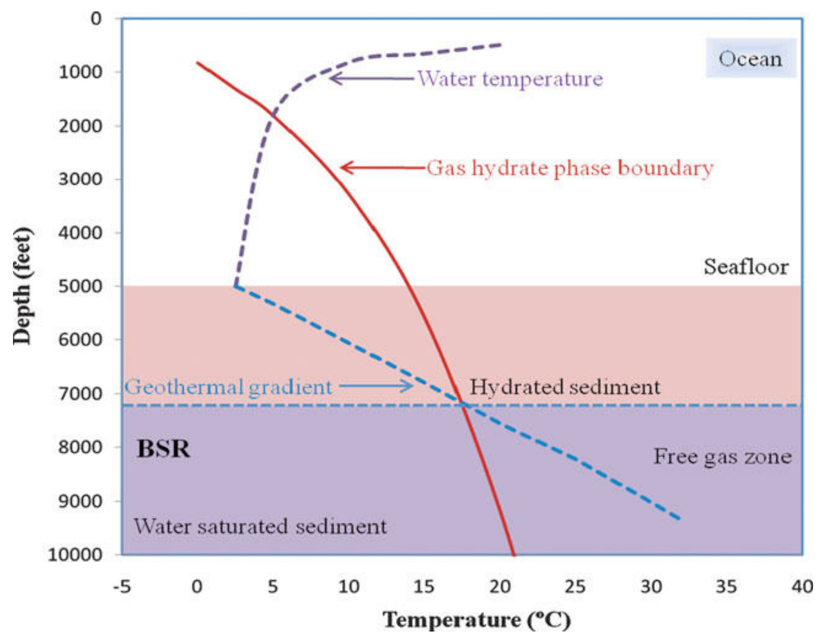
Dispersant Fate



- Deepwater Horizon oil spill included the injection of □771,000 gallons (2,900,000 L)
- DOSS was sequestered in hydrocarbon plumes at 1000-1200 m water depth and did not intermingle with surface dispersant applications.
- Persisted up to 300 km from the well, 64 days after dispersant applications ceased.
- Underwent negligible, or slow, rates of biodegradation in the affected waters.

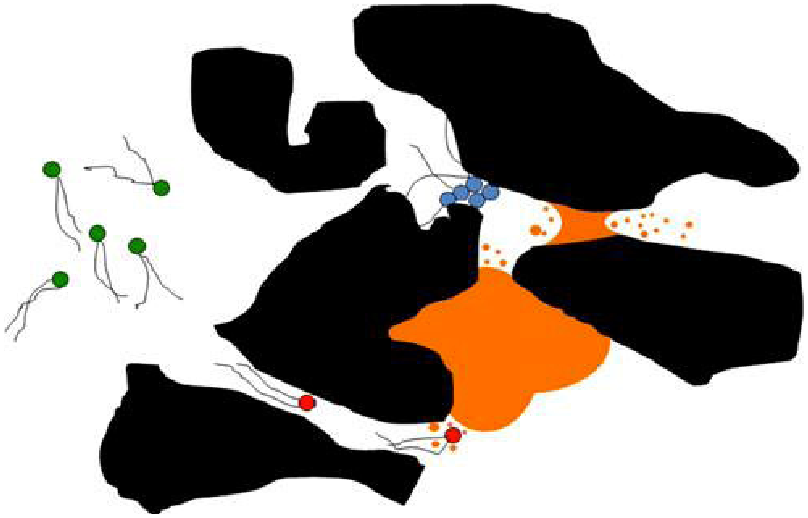
Hydrate behavior

- Location of hydrates in the system?
- Hydrates break free of oil droplets or be entrained?
- Surfactant-stabilized hydrates?
- Effect of oil compositional variations on droplet microstructure?
- Hydration thermodynamics (P,T effects) in deep-sea environments?



Oil/Detergent in/on Near-shore Environments

- Do oil droplets with dispersants adsorb to sediments or continue to “roll” on sediments and reach shallow waters, beaches and marshlands?
- Shallow water, higher temperature conditions release lighter fractions and form “tar balls”?
- Natural weathering, biostimulation, bioaugmentation, and physical removal of near-shore areas?



OIL/GAS BUDGET-UNKNOWNS AND KNOWNS

Hydrocarbon mass fractions produced from deepwater, shallow and surface O/G spills.

- **1. The soluble mass from gas moving from blow-out point to sea surface.**
- **2. Hydrates (gas) formed and fall back onto sea bed (melt then go in solution also?)**
- **3. Gas bubbling through the sea surface entering the atmosphere.**
- **4. *Soluble mass moving from oil-phase material in rising droplet plume.**
- **5. *Neutral-buoyancy droplet residue mass produced following solubilization of light-ends, it remains suspended to drift about at depth.**
- **6. *Negatively-buoyant droplet residue mass produced following solubilization which settles on the sea bed surface**
- **7. *Oil mass rendered negatively-buoyant from contact with suspended particulates. It settles onto the sea bed.**
- **8. *Soluble mass moving from floating oil surface slicks and/or near- surface mousse.**
- **9. *Neutral and negative-buoyant droplet residual produced following light-end solubilization and evaporation from surface slicks.**
- **10. Vaporized oil-phase material entering the atmosphere from surface slicks and near surface mousse.**
- **11. Floating oil-residue material of positive to near-neutral buoyancy (the slick).**
- **12. *Oil-phase aerosols ejected into the atmosphere by bursting bubbles and breaking waves.**

Denotes those processes influenced by dispersants.

Conventional Wisdom

- **OIL FLOATS WHEN SPILLED ON WATER!!!!**
- **WHEN IT DOES SINK, ATTACHMENT TO HEAVIER-THAN-WATER PARTICLES IS THE REASON!!!!**
  - **Organic debris (marine snow).**
  - **Copepod fecal matter.**
  - **Sediment and other particles from the River**
  - **Drilling mud solids.**
  - **Burned oil products.**
  - **Near shore sand carried off by high tidal currents.**

Reservoir and Fluid Composition

Reservoir Composition

Methane 77.8% atm. Vapor
Ethane 7.6% atm. Vapor

Liquids
C30+ 16.6% (wt) SG=1.007
C50+ 7.1 %(wt) SG=1.15

Sea Water SG=1.025
Oil API gravity 35.[SG=0.849]

Chemical Composition

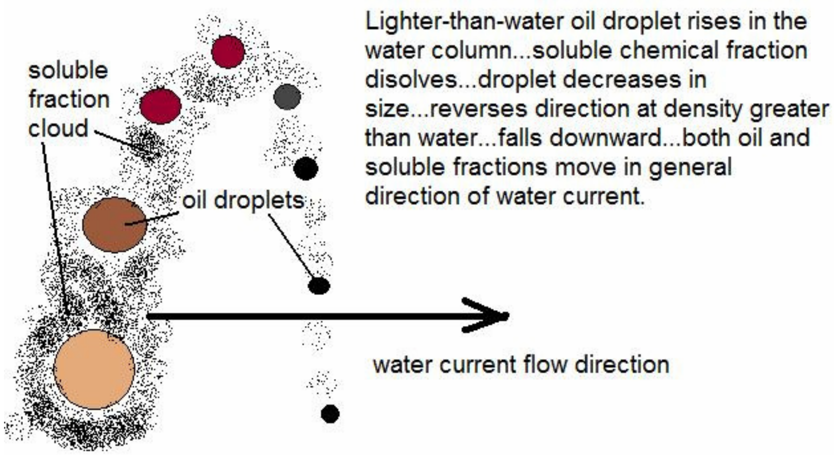
- PENTANE 0.63
- HEXANE 0.66
- TOLUENE 0.87
- BENZENE 0.88
- XYLENES ~0.87

- FRESH WATER 1.00
- SEA WATER 1.025

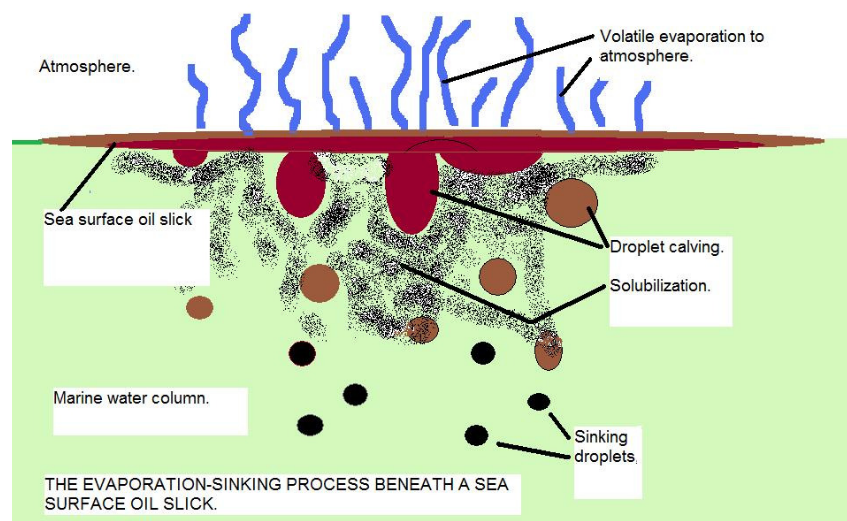
- ASPHALTENES 1.1 to 1.2
- NAPHTHALENE 1.15
- PHENANTHRENE 1.18
- BENZO-a- PYRENE 1.37

Droplet Transport in the Sea

Solubilization/Sinking

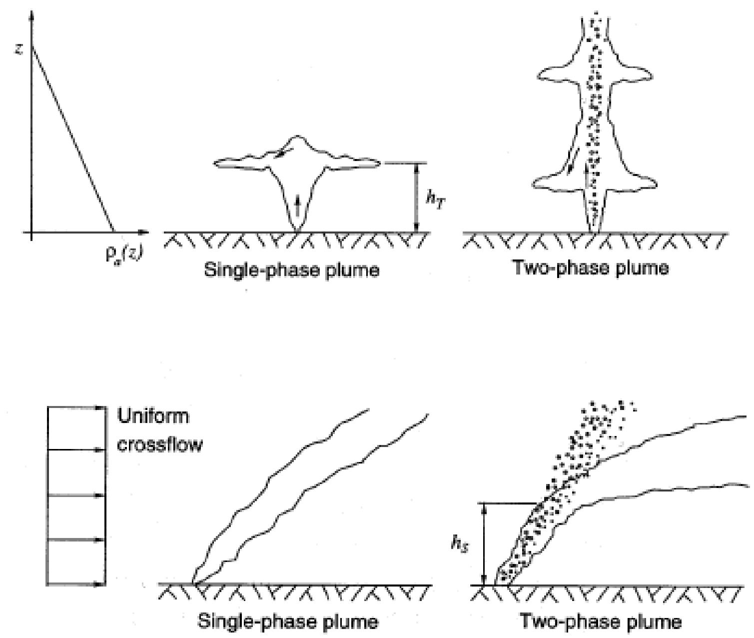


Evaporation/Sinking



Relevant Research Issues

- Deep Oil Spill modeling activity supported by MMS and Offshore Operators Committee, December 2004 report.
- Buoyancy driven separation of oil/gas plumes.
- Droplets 1 mm to size of discharge opening stratified by ambient conditions and current under the sea surface.
- Natural hydrates are thermodynamically stable and can influence bubble dissolution and rise.
- CDOG and DeepBlow models.

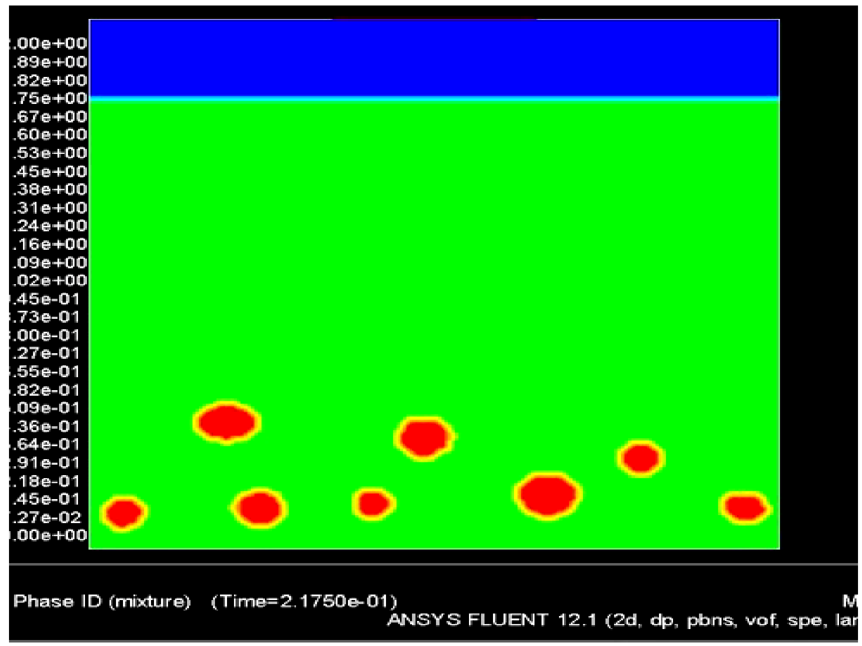


aration of plume phases due to ambient stratification (top) and cur
tom).

Advanced Multiphase Flow Models

Large Scale Convection current (right to left)

Evaporation/Sinking Simulated by FLUENT



Simulations courtesy of Prof. K Nandakumar's group at LSU

Unique Research Issues

- How does oil/gas/dispersant mixture behave at high Pressure and low Temperature?
- What are the fates of oil and dispersant?
- Hydrate behavior in the presence of dispersant?
- Need for good mass balance models incorporating reaction and transport in water column, bed-sediment and air for risk assessment and management.
- Experimental work on oil droplet movement in the water column needed. Evaporation/sinking and solubilization/sinking processes?
- Dispersant design for environmental compatibility (green surfactants, denser than seawater dispersants?).

Unique Research Issues

- T and ρ gradients, variability of transport coefficients and buoyancies of droplets as they age and the plumes move.
- Friction, adhesion, coalescence of coated oil droplets with sedimentary materials?
- Higher T and shallow water environment influence on oil/dispersant mixtures?