State-of-Science of Dispersants and Dispersed Oil: Degradation and Fate

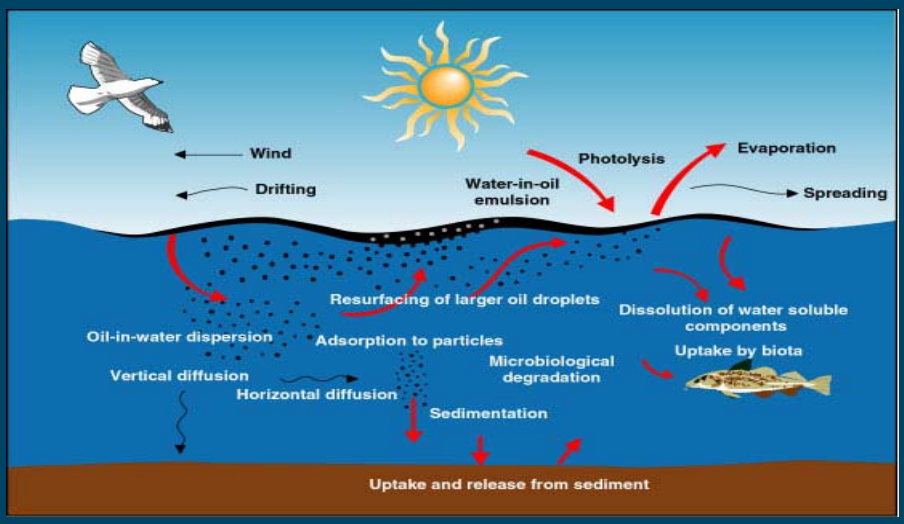
Nancy E. Kinner
Coastal Response Research Center
Center for Spills and Environmental Hazards

May 24, 2016
Flower Garden Banks Marine Sanctuary
Galveston, TX

Fate of Spilled Oil

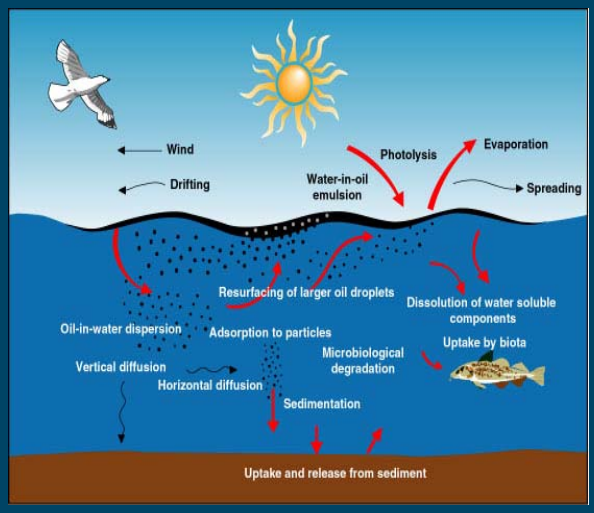
- "Big Picture" processes have not changed
- Oil weathers by:
  - Evaporation
  - Dissolution
  - Emulsification
  - Adsorption
  - Sedimentation
  - Degradation:
    - Photochemical
    - Microbial (biodegradation)

Weathering



Weathering

- Function of Environmental Conditions
  - Temperature
    - (H_2O, Air)
  - Wind
  - Oil Type
  - Currents, Tides



Today's Focus: Biodegradation

- Tomorrow:
  - Some newer findings: adsorption/sedimentation and evaporation

Basics

- Oil biodegradation research has been conducted extensively since 1960s and 1970s
- Bursts of oil degradation and fate research associated with several key oil spills:
  - *Exxon Valdez*, AK
  - Deepwater Horizon, GOM
- Methods for studying microbial processes have evolved greatly over time
  - Growing microbes on different food sources
  - Examine nuclear material (e.g., DNA, RNA)

Basics

- Field of microbiology has grown
- Number of environmental microbiologists has also grown
- Number of microbiologists focusing on oil biodegradation has been cyclic
  - Exxon Valdez $
  - DWH $
  - National Science Foundation (NSF) funded almost no oil studies
    - Mostly hazardous waste, water and wastewater treatment microbiology

Caveats

- Result: Surge of microbiologists and new techniques into oil biodegradation research during and after DWH
- Scale of focus is often different
  - Oil spill response community scientists have worked with dispersed oil
    - e.g., water accommodated fraction (WAF)

Caveats

- Oil spill is bad situation – goal is to protect resources at risk as best as possible
- Responders are choosing "least bad" option
- Dispersants chosen as response option to protect resources at risk and minimize shoreline clean-up
  - Not for biodegradation

Why am I giving this talk?

- Since 2004, CRRC co-director and CSE director
  - Oil spill focus
- Education in environmental engineering microbiology
  - Research in 1980s – 2000s on biodegradation of chlorinated solvents in groundwater
- Editorial board of Microbial Ecology 1998 to 2013
- Facilitated all State-of-Science of DDO panels
  - Including degradation & fate
- Degradation and Fate was a contentious topic (lots of passionately held opinions)

Biodegradation of Oil

- Many species/consortia of marine microbes (e.g., bacteria) degrade oil constituents
- Mineralization = Organic C to CO_2 (lots of organic C + O_2 CO_2 + H_2O + Energy (simple oil constituent))
- Electrons (e-) transfer from organic to O_2
  - Organic = e- donor (ED)
  - O_2 = electron accepter (EA)
- More complex oil compounds broken into simple compounds
  - Subsequent mineralization
- Oil constituents are naturally-occurring <u>not</u> exotic
  - E.g., natural oil seeps
- Oil constant biodegradation in oxygenated marine waters is relatively fast

Coastal Response Research Center

Environment without O_2 microbes use

- When O_2 is not present in environment, microbes use EA that is available
  - e.g., marine sediments with lots of organic C
  - e.g., Fe^{+3} NO^{-3}, SO_4^{-2}, other organics
  - Most marine sediments have abundance of SO_4^{-2}
  - Organic C + SO_4^{-2} → CO_2 + H_2S + Less Energy (simple oil constituents)
- When SO_4^{-2} or other organics are EAs, biodegradation is much slower
  - Result - oil constituents in sediments are typically buried faster than they are biodegraded
    - Classic papers - return to marshes, etc. years later (30+) and where no to very low O_2, oil constituents still present

Coastal Response Research Center

Degradation of Oil

- Microbes can biodegrade
- Most hydrocarbon
  - O2 is key
  - Constituents are degraded at different rates
    - Function of mass available/time, composition of constituents, nutrients available

Microbes Performing Biodegradation

- Lots with “Latin” names
  - Molecular methods (DAN/RNA) expanded knowledge of these
  - Most are ubiquitous
  - In low numbers until spill
    - GOM natural seeps
  - Succession in microbial community

Access to Oil

- Slicks have low available surface to volume
- Microbes work on droplet surface area or dissolved compounds
- All about access of microbes to oil constituents
- Droplets are key
  - Small droplets are best (Brakstad et al., 2015 (10 vs 30 µm)
- Chemical dispersants + turbulence foster small droplet formation

Sequential Biodegradation

- Lots of research on this
- Relatively non-controversial
- Solubilities of constituents vary
- Complexity varies
- Weathered oil hard to biodegrade (e.g., asphaltenes)

Dispersant Degradation

- Surfactants in dispersants (e.g., DOSS) biodegrade
  - Most studies on Corexit
- Some may degrade more slowly
- Some decay in sunlight – less known about by-products

Factors of Importance

- Nutrients – localized impact, but in water column less so
- Temperature – deep water cold water microbe adapted
- Trace metals
- Type of oil (light vs. heavy)

Current Disagreements

- Rates of biodegradation with chemical dispersion
  - Lab study conditions
  - Controls
  - Measuring oil constituents vs. surrogates
  - “Null results” bias
  - Dispersant and oil concentrations

Current Disagreements

- DWH is a rare event
  - Most spills are short-term and surface slicks

Current Disagreements

- What is the baseline comparison?
  - Chemical dispersion vs. ?
  - ? = slick
  - ? = physical dispersion
- Problem is physical dispersion is minimal especially of surface slicks

Current Disagreements

- Addition of chemical dispersants suppresses biodegradation vs. physical dispersion
  - ??

Current Disagreements

- Focus on Corexit
  - Other dispersants too

Bottom Line

- DWH is a rare spill
  - Most are surface slicks
- Chemical dispersants used to disperse oil
  - Protect resources at risk
  - Minimize shoreline oiling
- Physical dispersion for surface slicks is not typical
- Biodegradation of oil is enhanced by chemical dispersion vs. remaining as surface slicks