Fate of Dispersants: Chemistry

Efficacy and Effects of Dispersants in Oil Spill Response: Progress since the 2005 NRC Report

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Dispersants

• Mixtures of commercial surfactants in hydrocarbon solvent
• Surfactants are chemicals like soap and detergents
• Common dispersants – Corexit 9500, JD2000
Surfactant Basics

- Surfactants partition between target oil droplets and water
- In dilute solutions, surfactants that partition out are lost
- Once surfactants are lost, dispersed oil droplets are de-stabilized
Stabilization

- Depends largely on HLB - hydrophobic/lipophilic balance - dispersants nominally 10 (equal solubility in water/oil)
- Many dispersants are a mixture of surfactants – a common NA product consists of a very water soluble surfactant, a moderately soluble one and a highly oil soluble one
- Water soluble solvents are lost more rapidly
Dispersant increases heavy PAH solubility (4-, 5-, 6-ring)

Couillard et al, 2005
Low Salinity Effects

• Near-shore (estuine), sheltered waters (Baltic Sea, St. Lawrence Gulf), Arctic
• As salinity decreases, surfactants become more soluble and less able to stabilize oil
• Changes chemistry of water column—has large effects on ecological impacts
PAH solubility (2- and 3- ring) increases as salinity decreases for dispersed oil

Ramachandran et al, 2006, Mar Pol Bul, 52, pp1182-1189
Fingas et al, 2006, AMOP

• There is a three-way relationship between T, Sal and Effectiveness

• Total dispersed oil decreases with salinity
  • dispersants less effective in fresher water

• Dispersant effectiveness changes with temperature, but not linearly
Effects of Dispersant on Biodegradation Rate of Oil

Does dispersant increase biodegradation of oil?

– Several studies, evidence mixed.
– Many, many variables affect mineralization rates:
  • Temperature
  • Salinity
  • Nutrients
  • Oxygen Content
  • Energy
  • Local ecology (water column, shore, benthic, etc…)
Nyman et al, 2007, Env. Pollution, 149, pp227-238:

• Salt-water microcosms simulating salt march.
• Total petroleum hydrocarbons (TPH) biodegradation not affected by dispersant (Corexit 9500) or by shoreline cleaner (Corexit 9580)

BUT:
- low oxygen environment
- no added nutrients
Water-column microcosms, salt water, high oxygen, no nutrients
Two types of dispersant enhance biodegradation rates
Dispersed oil also found to mineralize faster at low temps

Temperature = 20° C

(a) Total Alkanes, Undiluted
- No Disp: $C = 71.88 \exp(-0.17t)$
- C9500: $C = 50.06 \exp(-0.66t)$
- JD2000: $C = 46.38 \exp(-0.21t)$

(b) Total Alkanes, Diluted 1:10
- C9500: $C = 4.16 \exp(-0.23t)$
- JD2000: $C = 2.95 \exp(-0.35t)$

(c) Total PAHs, Undiluted
- No Disp: $C = 23.60 \exp(-0.13t)$
- C9500: $C = 16.43 \exp(-0.19t)$
- JD2000: $C = 14.68 \exp(-0.15t)$

(d) Total PAHs, Diluted 1:10
- C9500: $C = 1.29 \exp(-0.218t)$
- JD2000: $C = 0.90 \exp(-0.233t)$
Organisms as chemical sensors?

Many studies of dispersed oil on organisms.

Can use as a “sensor” for oil concentrations, particularly PAHs

Ramachandran et al, 2006
Summary

- Much research since NRC report in 2005
  - Conditions: low salinity, low temperature
  - Biodegradation: effects of varying conditions complex, still not very predictable
  - Chemistry ↔ Toxicology

- Understanding not complete:
  - Effects of chemistry on resurfacing
  - Effects of different surfactant mixes on oil chemistry
Thank-you!

Questions?