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Role of dispersants in oil spill response

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Overview of this presentation

- Biodegradation is the eventual fate of spilled oil that is not collected or burnt
  - Oil is an unusual food for microbial growth
    - It is essentially insoluble
      - So degradation takes place at the oil water interface
    - It is not nutritionally complete (low N, P, Fe, etc.)
    - There are competing processes, especially photochemistry and emulsification, that inhibit biodegradation
- Key to rapid removal of oil is dispersion to tiny droplets so that biodegradation is encouraged
  - Failing that, fertilizers will stimulate the biodegradation of oil that reaches shorelines, but degradation will take months to years instead of days to weeks
- Experiments aiming to inform clean-up operations and environmental assessments must be done at environmentally relevant concentrations

Lee, K., Nedwed, T., Prince, R. C. and Palandro, D. (2013) Lab tests on the biodegradation of chemically dispersed oil should consider the rapid dilution that occurs at sea. Mar. Pollut. Bull. 73, 314-318.

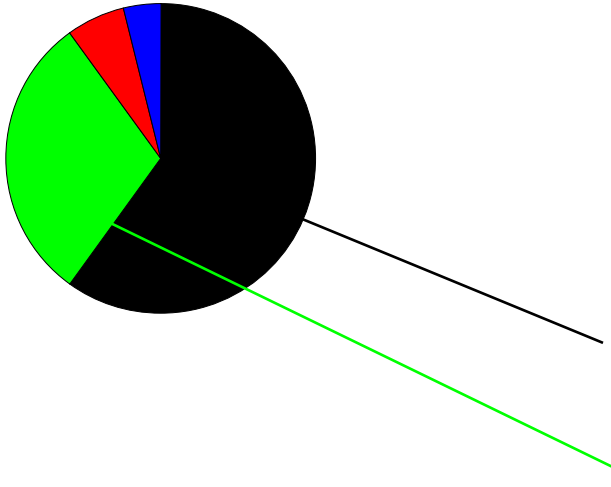
Oil in the environment

- Oil has been part of the biosphere for millions of years
  - The average age of commercial crude oils is 100 million years
- Natural seeps deliver ~600,000 tonnes of oil into the world's oceans every year
  - Estimates range from 200,000 to 2,000,000 tonnes per year
- Human activities approximately double this
  - Major inputs are non-point sources
  - Ship spills were 4,000 tonnes in 2014, but the Deepwater Horizon tragedy (2010) released 435,000 tonnes

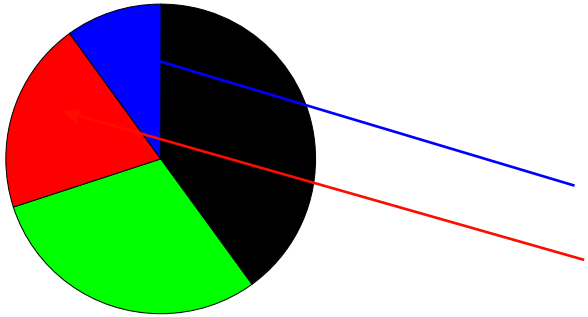
National Research Council (1985) Oil in the Sea III
http://www.nap.edu/catalog/314/oil-in-the-sea-inputs-fates-and-effects

Composition of crude oil

Light North Sea Oil



Heavy North Sea Oil



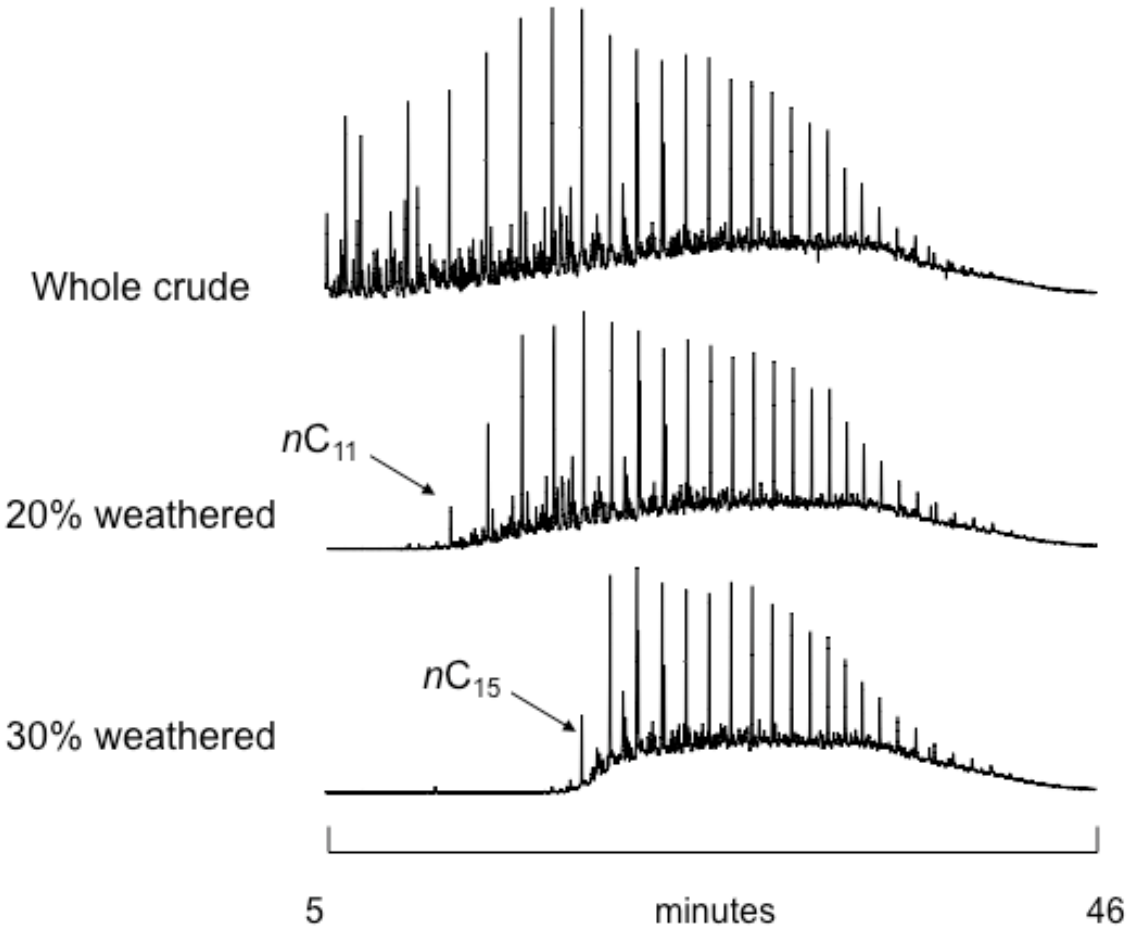
Crude oils are principally hydrocarbons - and these can be analyzed by gas chromatography

- Saturated molecules
  - + Paraffins
  - + Naphthenes
- Aromatics

Also some heteroatom-containing species
- asphaltenes and
- resins - that give the color to crude oils

B. P Tissot, D. H. Welte (1983) Petroleum Formation and Occurrence Springer

Evaporation happens quickly



- Rate and extent depends on oil thickness

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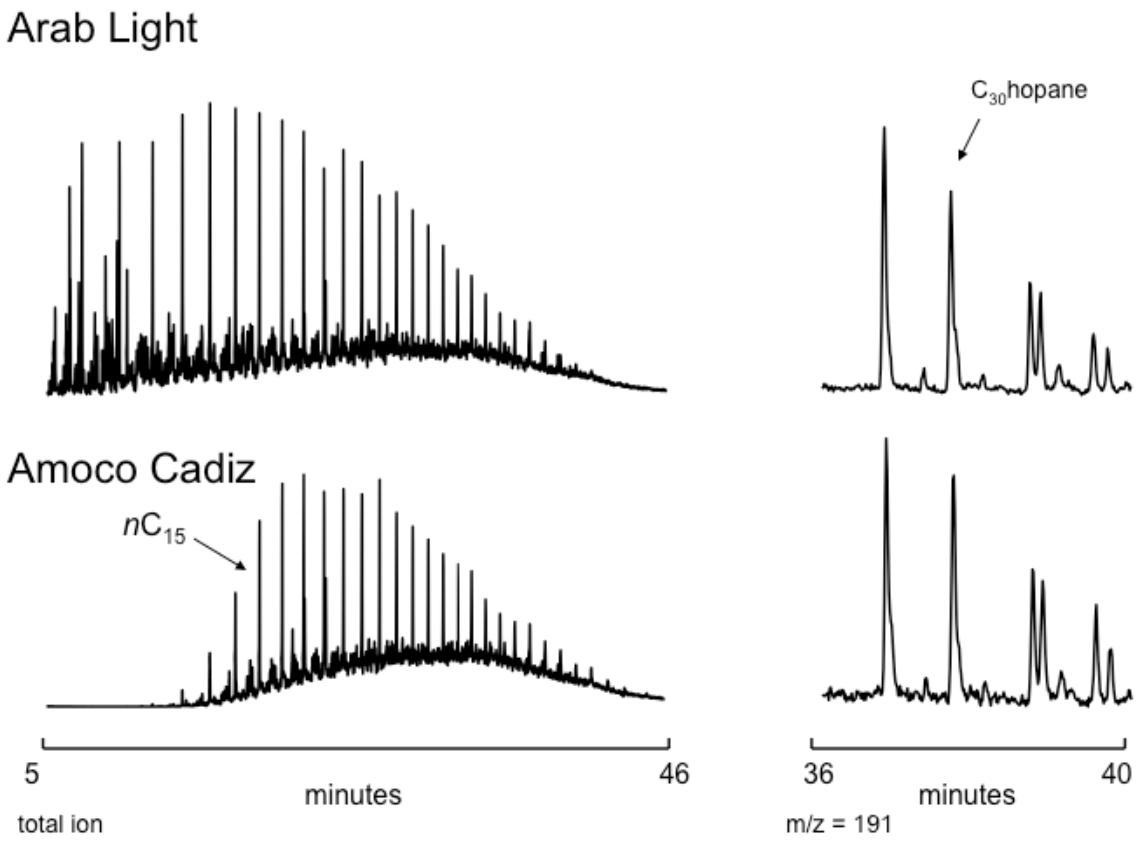
Amoco Cadiz spill (1978)



- Oil collected as soon as it washed ashore
- Provenance indicated by biomarkers

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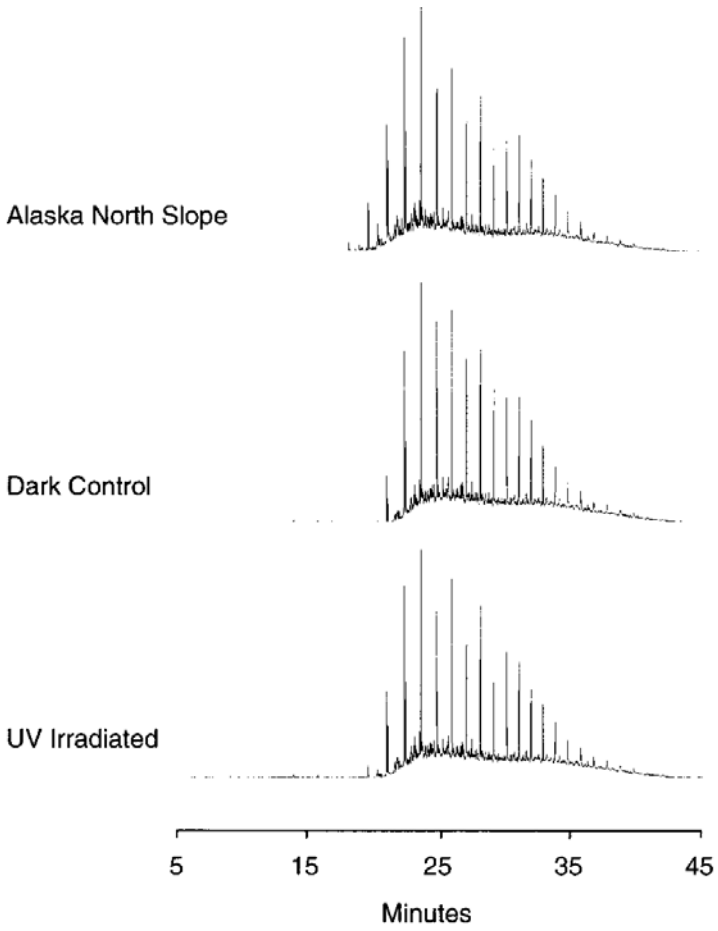
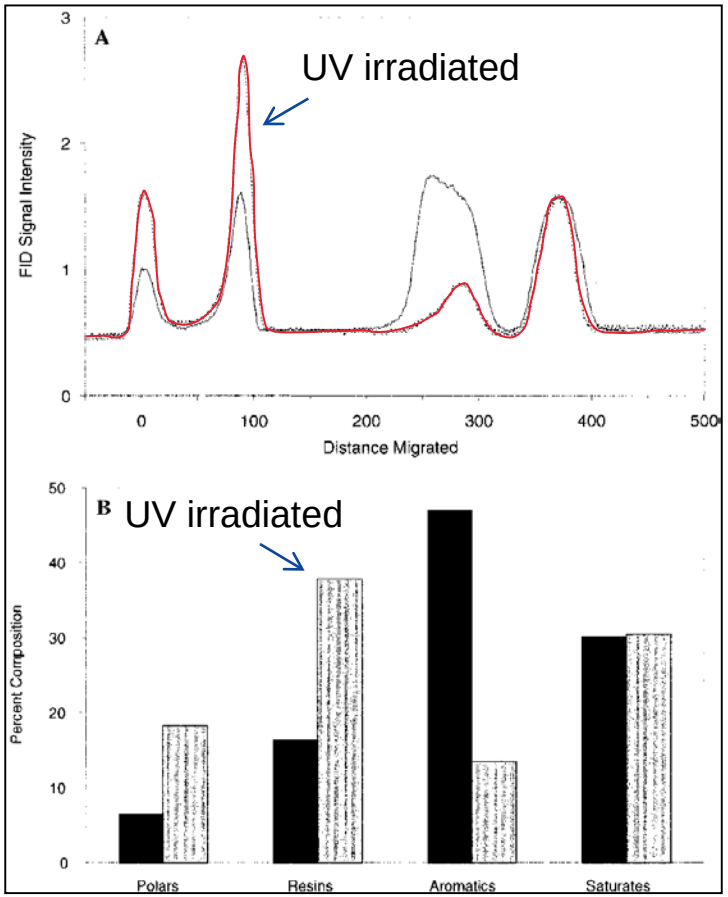
Photochemistry complicates things

- Photochemistry oxygenates aromatics

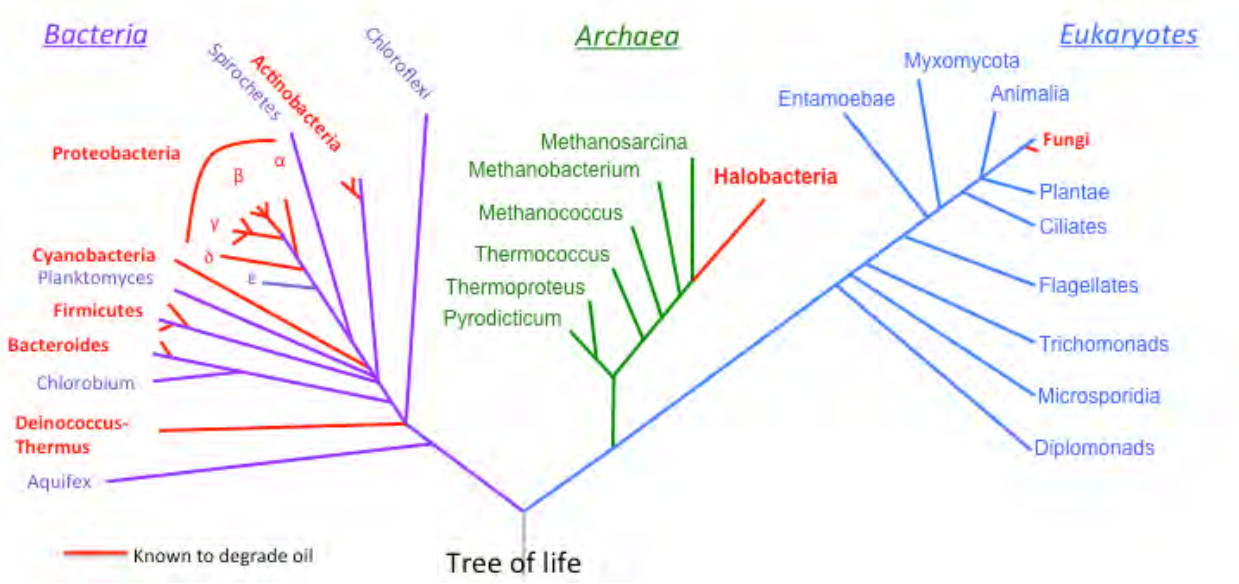




Garrett, R. M., Pickering, I. J., Haith, C. E. and Prince, R. C. (1998) Photooxidation of crude oils. Environ. Sci. Technol. 32, 3719-3723.

Oil biodegradation

- Species of >175 prokaryotic genera in 7 phyla of Bacteria and Archaea can grow on oil – so can many fungi



- They are found in all marine environments, including the Poles and the ocean's depths

Hazen and Prince (2016) Marine oil biodegradation Environ. Sci. Technol. in press

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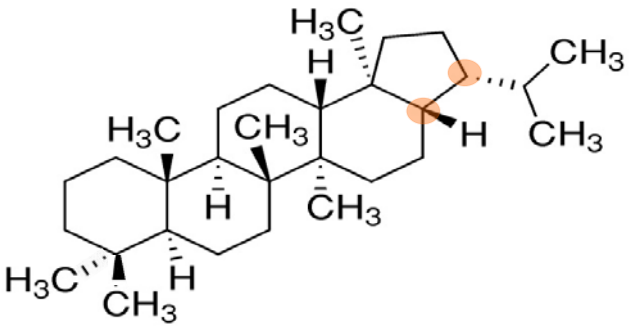
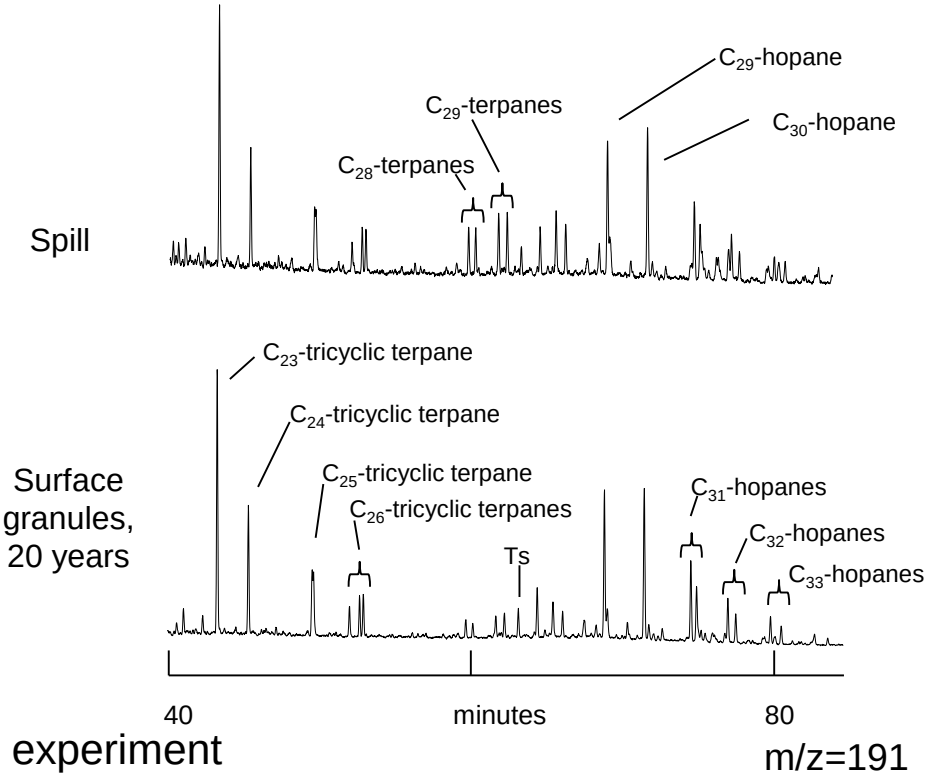
Quantifying biodegradation

- Because oil is insoluble, representative subsamples cannot easily be taken from an experiment as it proceeds
  - Best that each time-point be a unique experiment.
- Precision and accuracy are dramatically improved by using conserved internal compounds within the oil as benchmarks from which to judge biodegradation
  - We routinely use hopane

17α(H),21β(H)-hopane

C_{30}-hopane





Prince et al (1994) Environ. Sci. Technol. 28, 142-145.
Prince et al. (2002). Mar. Pollut. Bull. 44, 1236-1242.

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Oxygen?

- Oil is known to be degraded under both oxic and anoxic conditions
  - Biodegradation seems fastest under aerobic conditions, and most of the world's oceans are oxic
  - Complete aerobic biodegradation requires 1.5 O_2 molecules per -CH_2- moiety for complete mineralization of the hydrocarbon to CO_2 and H_2O
  - Taking account of molecular weights, each ppm of hydrocarbon requires 3.4 ppm of oxygen for complete aerobic biodegradation
  - Typical surface seawater [O_2] is >6.4ppm – enough for 1.9 ppm hydrocarbon even without mixing

Oil biodegradation

- But oil is an unusual ‘food’
  - It is essentially insoluble
    - So microbes must carry out their biodegradation at the oil water interface
  - It does not provide other elements (N, P, Fe, etc.) essential for microbial growth
    - So microbes must rely on the sea to provide these nutrients, and if oil concentrations are high their growth is likely to be limited by lack of these essential nutrients
- These two limitations provide two routes for intervention to stimulate biodegradation

Maximize the surface area for microbial access

- Dispersants reduce the interfacial tension between oil and water, allowing relatively minor turbulence to disperse oil into the water column
  - Typically applied at a nominal ‘dose’ of 5 gallons per acre (aiming for dispersant to oil ratio of 1:15)
    - They are composed of food grade surfactants dissolved in hydrocarbon solvents
    - Their inherent toxicity is typically about the same as ‘dish-washing’ liquids, but dispersed oil is significantly more bioavailable than a floating slick, and thus more toxic
      - We will return to this to discuss Net Environmental Benefit Analysis of oil spill response options

Prince, R. C. (2015) Oil spill dispersants: boon or bane? Environ. Sci. Technol. 49, 6376–6384.

Dispersant application

Airborne Support

And at depth

1.1 million gallons of Corexit 9500 used at Deepwater Horizon well-head

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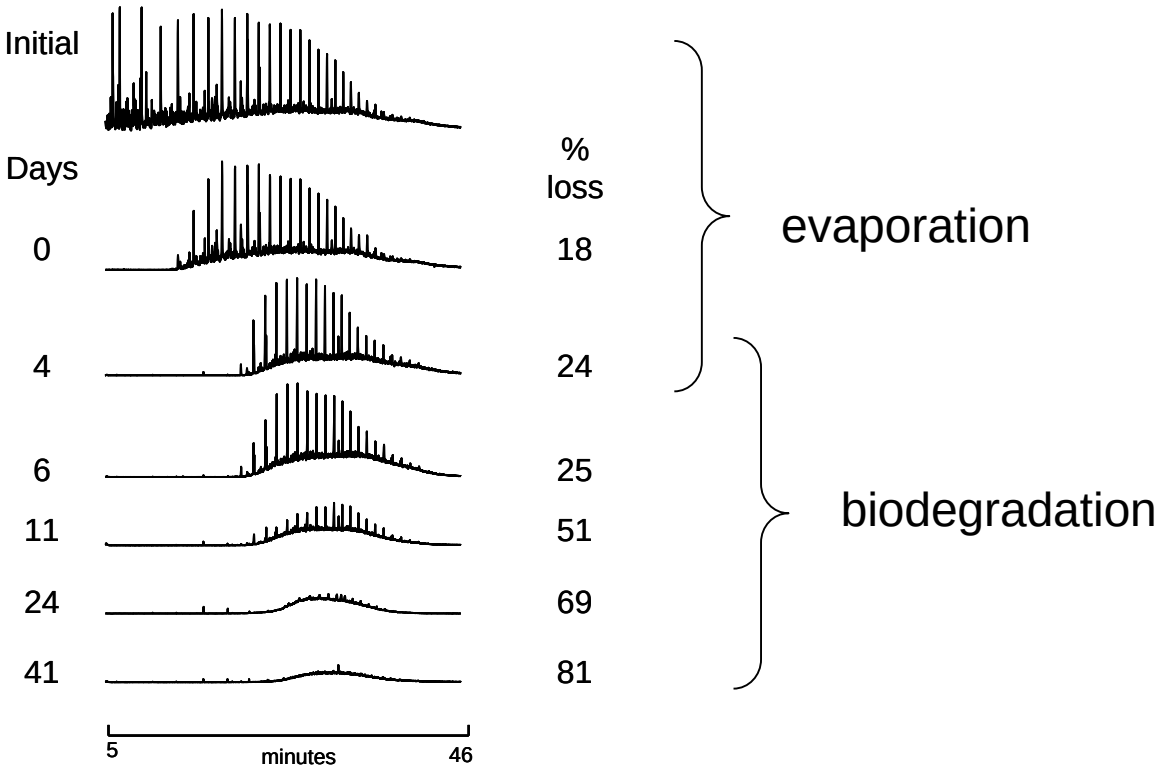
Maximize the surface area for microbial access

- Once dispersed as tiny droplets (<70μm), oil becomes neutrally buoyant, and the droplets diffuse apart
  - This diffusion is hampered in standard lab tests, and droplets re-coalesce and form floating slicks
  - In the sea, concentrations soon fall to the sub-ppm level, and little oil re-floats
    - At such concentrations, there are enough nutrients and oxygen for microbial growth

Prince, R. C., McFarlin, K. M., Butler, J. D., Febbo, E. J., Wang, F. C. Y. and Nedwed, T. J. (2013) The primary biodegradation of dispersed crude oil in the sea. Chemosphere 90, 521-526.
McFarlin, K. M., Prince, R. C., Perkins, R. and Leigh M. B. (2014) Biodegradation of dispersed oil in Arctic seawater at -1C. PLoS ONE 9(1): e84297. doi:10.1371/journal.pone.0084297

Oil biodegradation

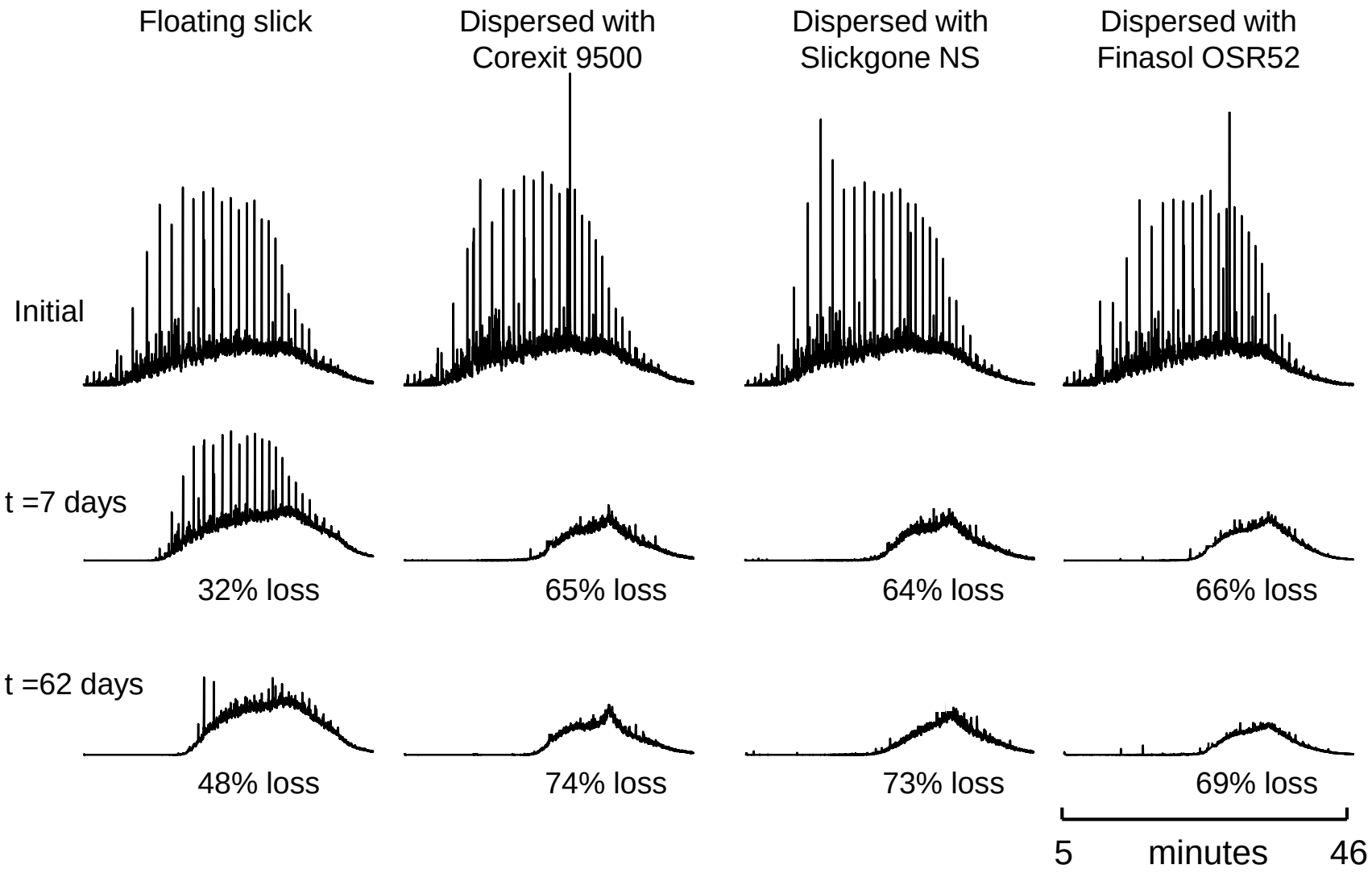
- The aerobic biodegradation of 2.5ppm Alaska North Slope crude oil at 8C, no added nutrients



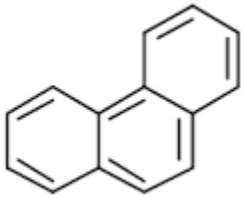
GC/MS total ion

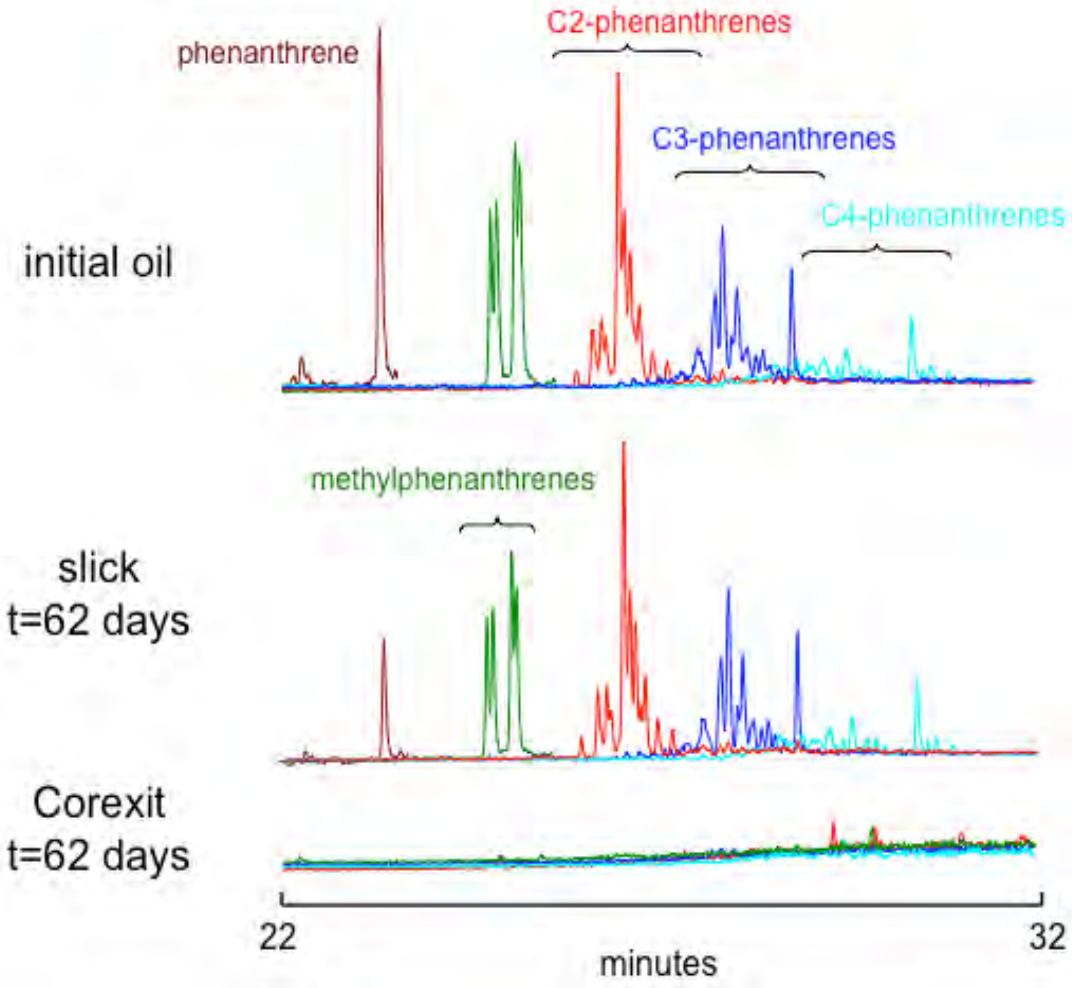
Note 50% loss in about 11 days, another 50% of remainder in about 30 days

Dispersants do stimulate biodegradation



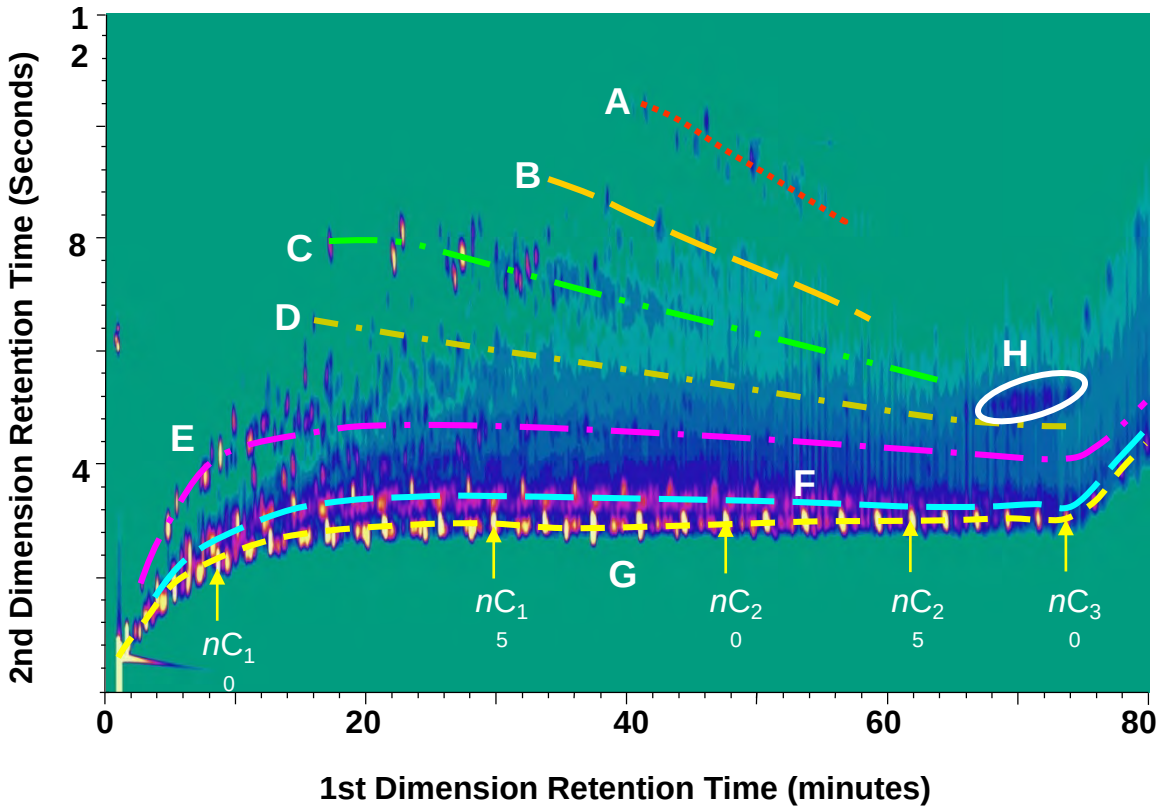
Phenanthrenes





m/z = 178, 192, 206, 220, 234

Oil composition

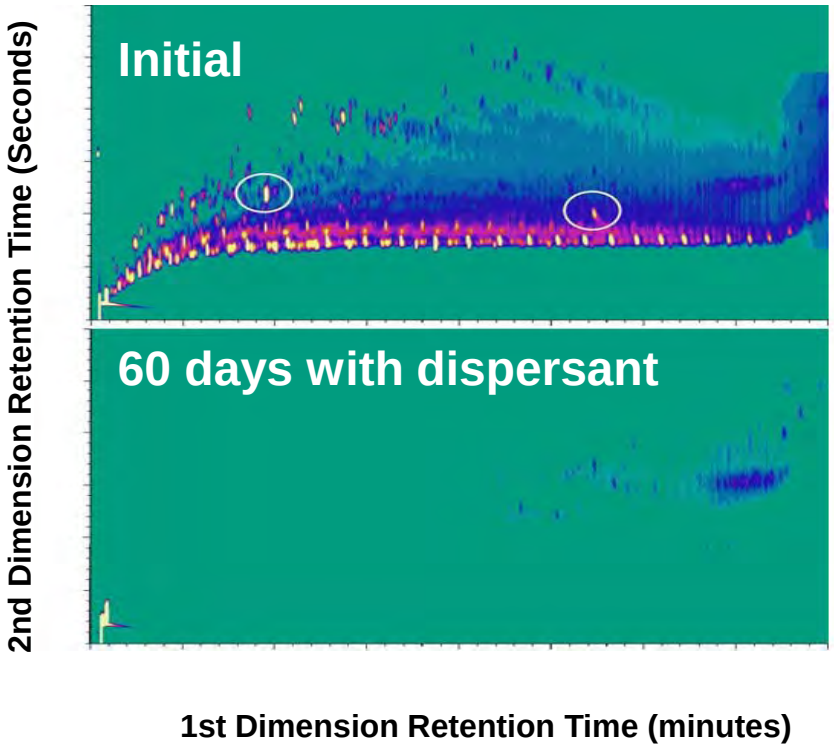


A: 3-ring aromatic series. B: 2- ring aromatic + 1-saturate ring or 5-saturate ring series. C: 2-ring aromatic or 4-saturate ring series. D: 1-ring aromatic + 1-saturate ring or 3-saturate ring series. E: 1-ring aromatic or 2-saturate ring series. F: 1-saturate ring series. G. alkanes – representative n-alkanes are identified. H: hopanes

GCxGC

Oil biodegradation

- Biodegradation extends to all hydrocarbon components except the hopanes



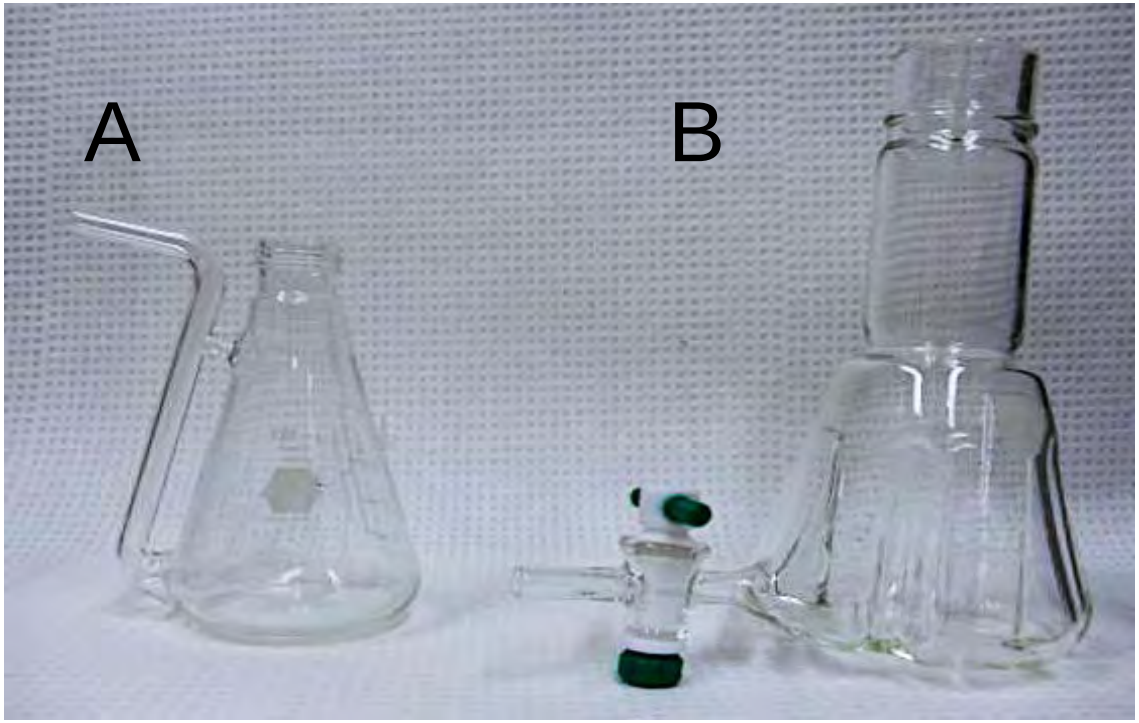
2.5 ppm oil
New Jersey seawater
no additions

hopanes are the last
to be biodegraded

Prince, R. C., McFarlin, K. M., Butler, J. D., Febbo, E. J., Wang, F. C. Y. and Nedwed, T. J. (2013) The primary biodegradation of dispersed crude oil in the sea. Chemosphere 90, 521-526.

Dispersant testing – USEPA methods

- There are literally hundreds of proposed ways of testing dispersants for their ability to disperse
  - The USEPA requires a shake flask test, and has proposed moving to a baffled flask.



Dispersant testing

- The tests for dispersant efficacy are excellent for testing efficacy, but completely unsuitable for tests of biodegradation –
  - If all the oil was dispersed, the water would have 833 ppm oil
  - At such concentrations, dispersed droplets collide, coalesce, and float
- On the other hand, oil concentrations at sea under successfully dispersed slicks fall to <1ppm within an hour
  - The concentration in the dispersed deepwater ‘plume’ from the Macondo blowout was < 1ppm
  - Concentrations below about 5ppm are invisible to the human eye – although readily detected by fluorescence

Shorelines

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If oil reaches a shoreline

- The goal is still to increase the surface area for biodegradation, so physical removal, perhaps by washing and skimming the oil, is first priority
- Then fertilizers should be applied to partially relieve nutrient-limitation without causing adverse environmental impacts
  - Oleophilic, slow-release and soluble fertilizers all potentially have roles to play
- Oleophilic and slow release fertilizers were used in the bioremediation strategy following the *Exxon Valdez* spill

Bioremediation only used on thin oil

- Either on lightly oiled shores, or after flushing as much oil as possible with water

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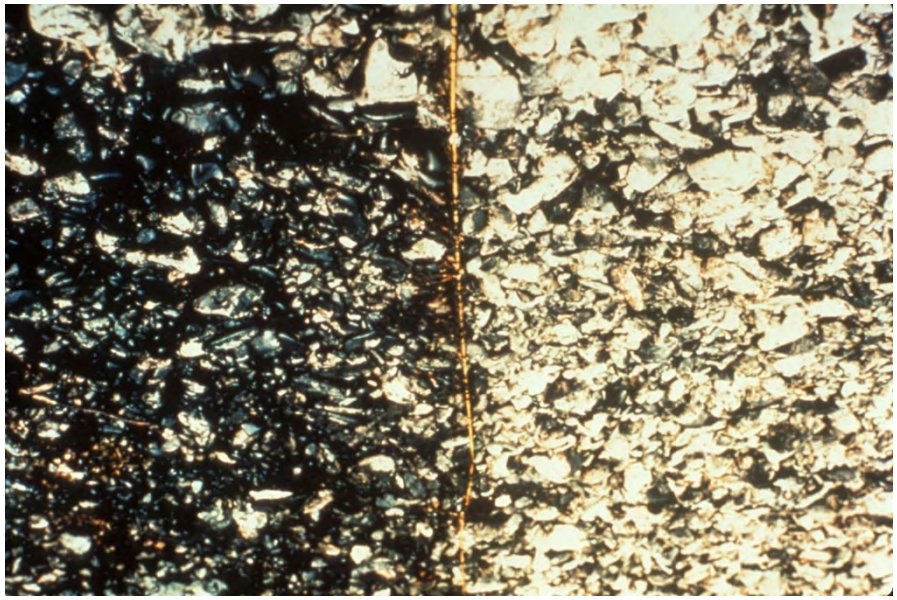
Inipol was dramatically effective

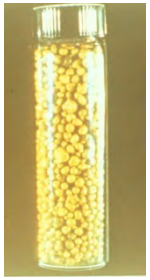
Inipol

Inipol was used on surface oil



Inipol EAP22

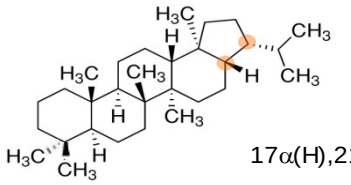
Customblen was used for subsurface oil



Customblen

Oil biodegradation was stimulated

- Using a resistant molecule in the oil as a conserved internal marker, and using simple proportion, one can overcome the inherent heterogeneity of the natural world
- Here we used hopane

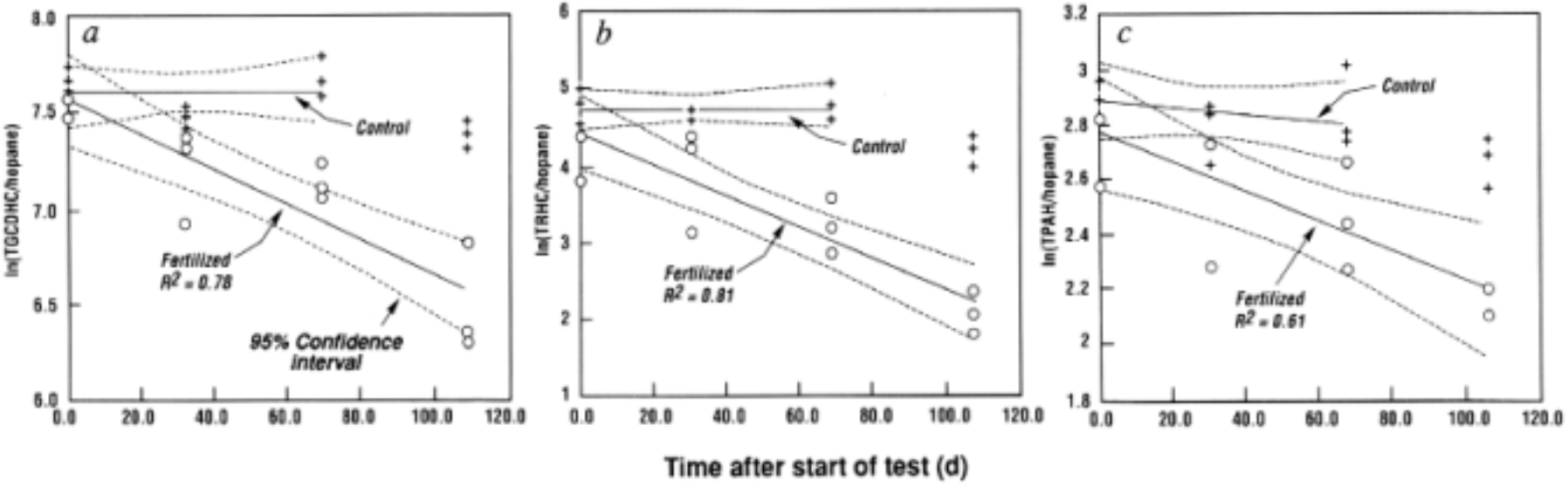


17α(H),21β(H)-hopane

Total detectable hydrocarbon

Total alkanes

Total polycyclic aromatics



Bragg, J. R., Prince, R. C., Harner, E. J. and Atlas, R. M. (1994) Effectiveness of bioremediation for the Exxon Valdez oil spill. Nature 368, 413-418

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Net environmental benefit analysis

- The goal of all oil spill response is to have a beneficial effect on the environment
- Dispersing an oil slick may increase local toxicity to organisms near the sea surface, including fish larvae, but benefits include a dramatic increase in the rate of oil biodegradation
  - Half-life of dispersed oil is measured in a few weeks, of beached oil a few years if not picked up
  - Undispersed oil is subject to emulsification and photo-oxidation, both of which tend to inhibit biodegradation and prolong residence of oil in the environment