Science Advisory Board for Contaminated Sites in BC
13th Annual Workshop and Conference – September 27, 2023

Natural Attenuation of Petroleum Hydrocarbons in Marine Environments – An intensive literature review

Will Gaherty, M.S. P.Eng. F.E.C.

PGL Environmental Consultants, Vancouver

Land Acknowledgement

I am presenting from, and I live and work on the traditional and unceded territories of the Squamish (Sḵwx̱wú7mesh Úxwumixw), Musqueam (xʷməθkʷəy̓əm) and Tsleil-Waututh (səlilwətaɬ) peoples.

In the spirit of reconciliation, I acknowledge

- *the genocidal actions of my settler ancestors and*
- *my own biases.*

I strive to do better.

This presentation does not address First Nations knowledge, largely because it is not represented in the literature and primary source consultation was not part of the scope.

30,000 FEET

- Consortia of obligate hydrocarbon-consuming bacteria, archaea and fungi fully mineralize hydrocarbons C44 minus in every studied marine environment
- The fate of generally C45 plus is not identified in the literature
- The effect of environmental conditions on the attenuation rate is reasonably understood qualitatively

WHERE DID THIS COME FROM?

- Five reviewers and curated list of 202 papers and documents for Fisheries & Oceans Canada for a Canadian Science Advisory Secretariat program
- This talk today is not endorsed by nor does it necessarily reflect the opinion of either of these organizations, it represents the conclusions of the reviewers
- The purpose of the review was to identify literature consensus and make it accessible to a non-expert audience in the context of spill response
- Extracted from a dense 50-page report

HISTORY

The normal progress of scientific understanding of marine oil behaviour and fate was vastly accelerated by the advent of genomics tools coupled with the catastrophes at Prince William Sound (1989) and Deepwater Horizon (2010). The genomics tools allow us to probe for enzymatic systems used by organisms to metabolize oil.

Some good came from these terrible events, they gave us knowledge we can use to manage future events and catastrophes better.

CATASTROPHES

- Exxon Valdez – release of roughly 40million litres (16 Olympic swimming pools) of crude oil (34,600T) affecting roughly 800km of shoreline in Prince William Sound. By 2015, it is estimated that roughly 56T remained.
- Deepwater Horizon – Blowout of in the Gulf of Mexico in 2010 that released an estimated 750million liters (substantially overtop the Rose Bowl) of hydrocarbons over several months. The oil contained substantial quantities of dissolved petroleum gases and originated from a wellhead at roughly 1000m below the surface.

From: https://www.britannica.com/event/Deepwater-Horizon-oil-spill

From: https://www.fisheries.noaa.gov/national/habitat-conservation/10-years-noaas-work-after-deepwater-horizon-oil-spill-timeline

TERMINOLOGY

“Stranding” generally refers to situations where oil phase enters the pore space of sediments, and ignores the reversibility of this situation

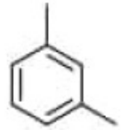
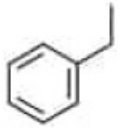
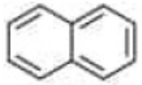
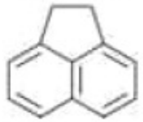
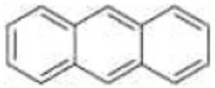
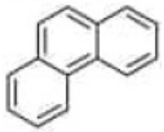
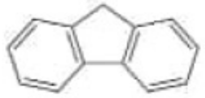
OVERVIEW

- What is oil
- Elements of natural attenuation
  - Abiotic
  - Biodegradation
  - Toxicity effects
- Spill response
- Summary

From: Heiltsuk Tribal Council (2017)

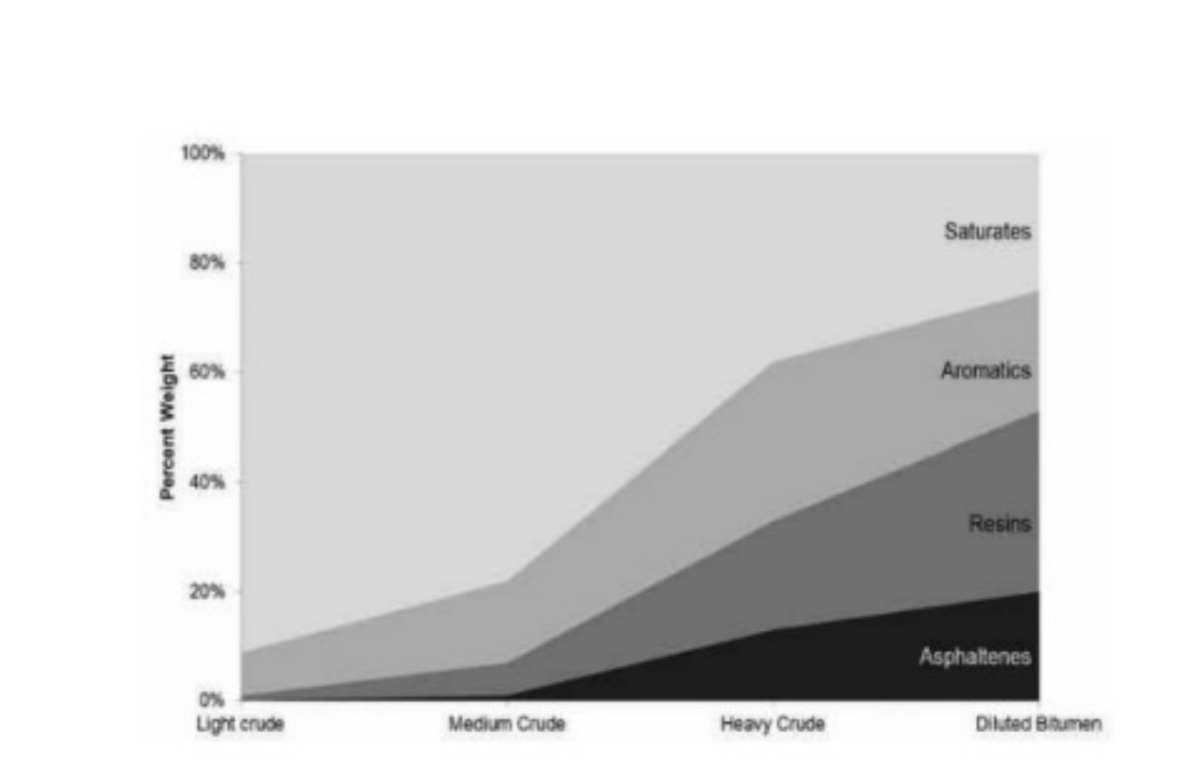
OIL

- Refined products contain mixtures of hundreds to thousands of compounds, mostly CH, some O,N,S, saturates and rings
- grouped in “families”, typically saturates, aromatics, resins, asphaltenes

Type	Parent compound structure	Compound
One-ring		*m*-xylene
		Ethylbenzene
Two-rings		Naphthalene C_1–N C_2–N C_3–N
Three-rings		Acenaphthylene
		Acenaphthene
		Anthracene
		Phenanthrene C_1–P C_2–P
		Fluorene C_1–F C_2–F

Examples of common compounds from A Gomes et al. (2022)

CRUDE OIL COMPONENTS



From National Academies of Sciences, Oil in the Sea IV: Inputs, Fates, and Effects (2022)

PERSISTENCE VS. MOLECULAR WEIGHT

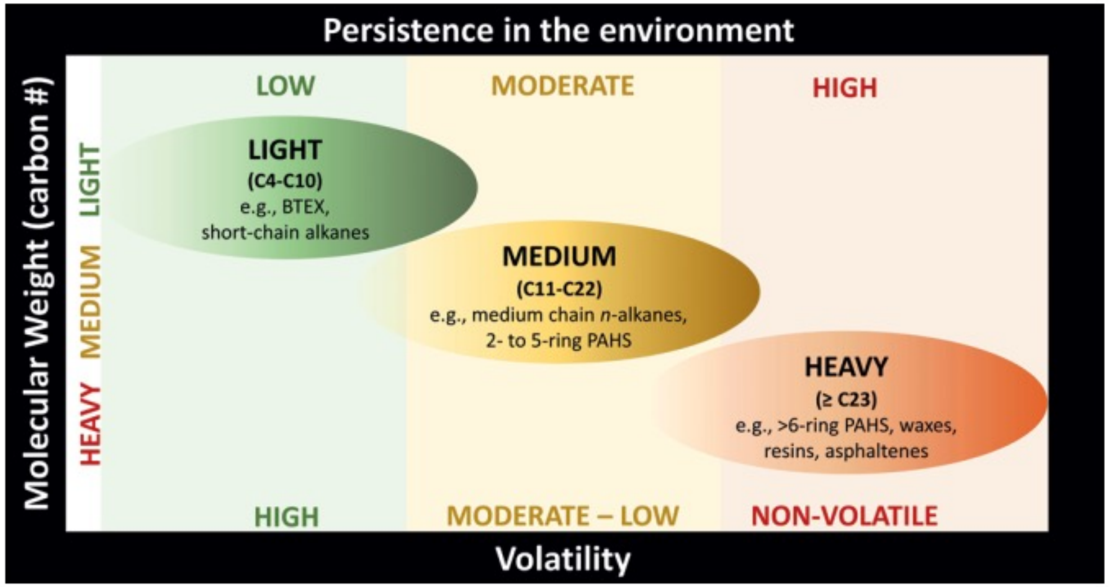


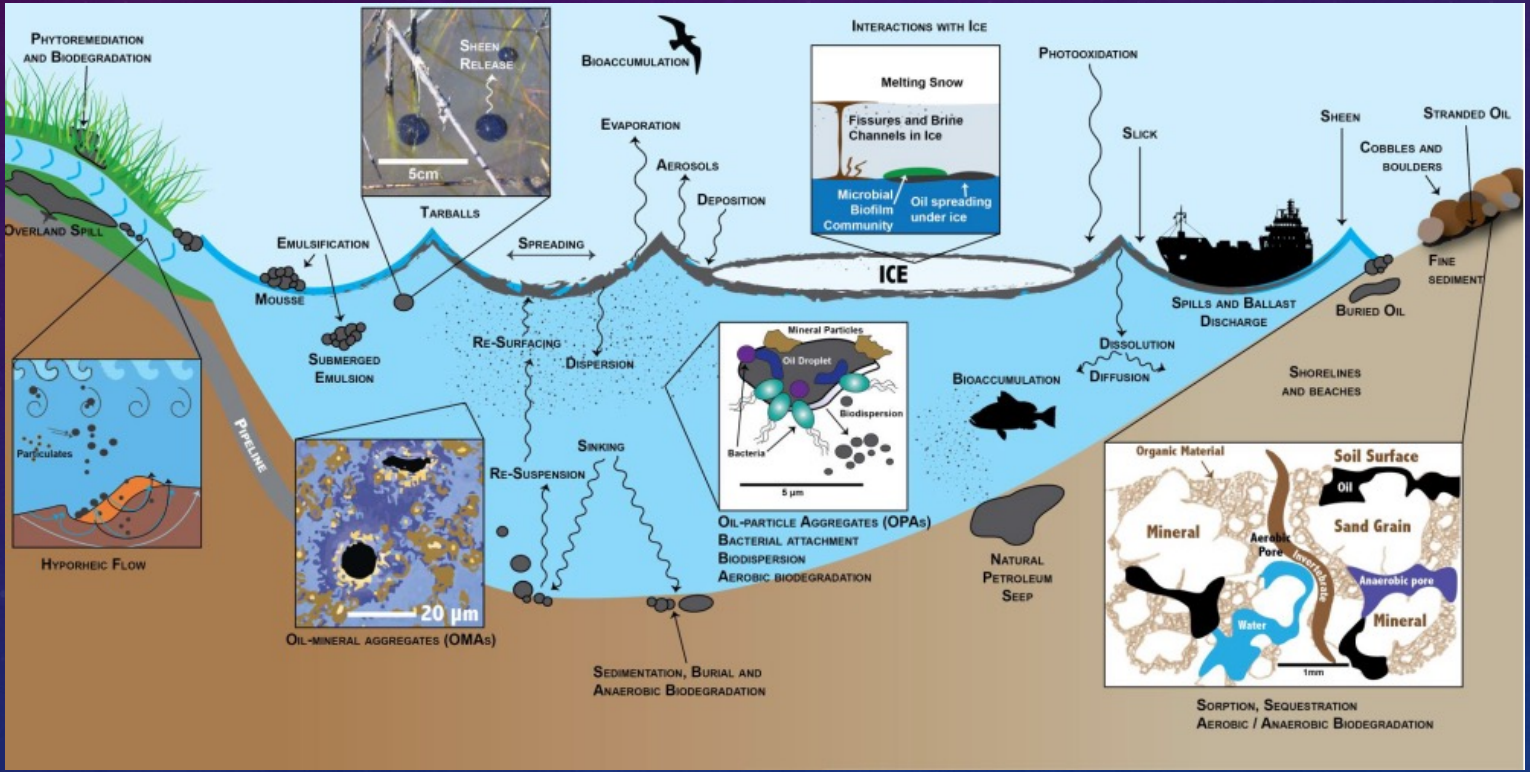
FIGURE 5.2 High-level overview of the relative persistence of oil components in the environment in relation to molecular weight and volatility.

From National Academies of Sciences, Oil in the Sea IV: Inputs, Fates, and Effects (2022)

OIL RELEASE PROCESS

- Floats to the surface - density
- Soluble components dissolve – solubility, mixing
- Dispersion into droplets – viscosity, dissolved gases, energy
- Spread at surface – physical characteristics, surface conditions
- Volatilization – vapour pressure, surface area
- Degradation - molecular weight
- Mixing/droplets/emulsification – physical characteristics, surface conditions
- Degradation – population increase, consortial succession
- Photodegradation (oxidation by free radicals) – sunlight incidence
- MOS formation
- Colonization of oil by degraders
- Sinking due to density changes, aggregation with minerals – density, minerals presence
- Stranding

PROCESSES



Taken from Royal Society of Canada, The Behaviour and Environmental Impacts of Crude Oil Released into Aqueous Environments (2015),

ABIOTIC PROCESSES

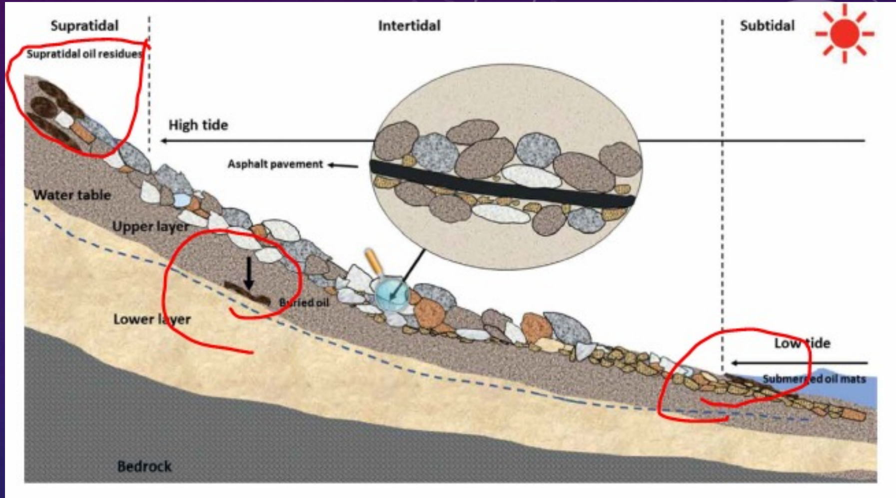
- Volatilization
- Dissolution
- Dispersion
- Photooxidation
- Emulsification
- Sinking
- Stranding on land
- Stranding on ice

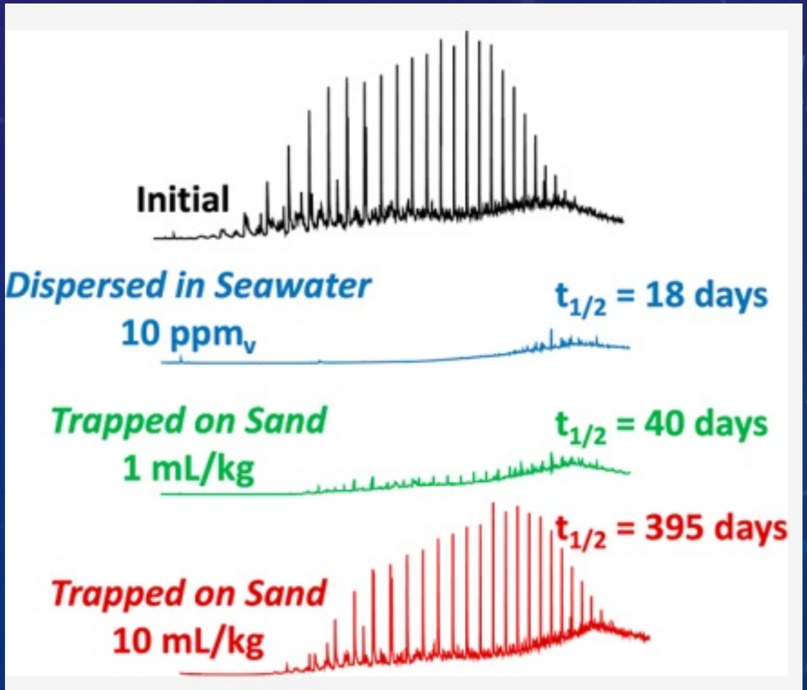
From National Academies of Sciences, Oil in the Sea IV: Inputs, Fates, and Effects (2022)

OIL STRANDING

- Critical grain size issue:
  - Fine excludes oil
  - Coarse leaves it exposed to degradation
  - Sands allow penetration and tend to retain
- Structure of beaches matter – layered beaches more likely to retain oil vs. non-layered
- Dryer soils easier to penetrate
- Carbonaceous vs. silicate – carbonaceous appear to facilitate degradation
- Wave exposure (mixing, nutrient delivery, reduction of hypersalinity)

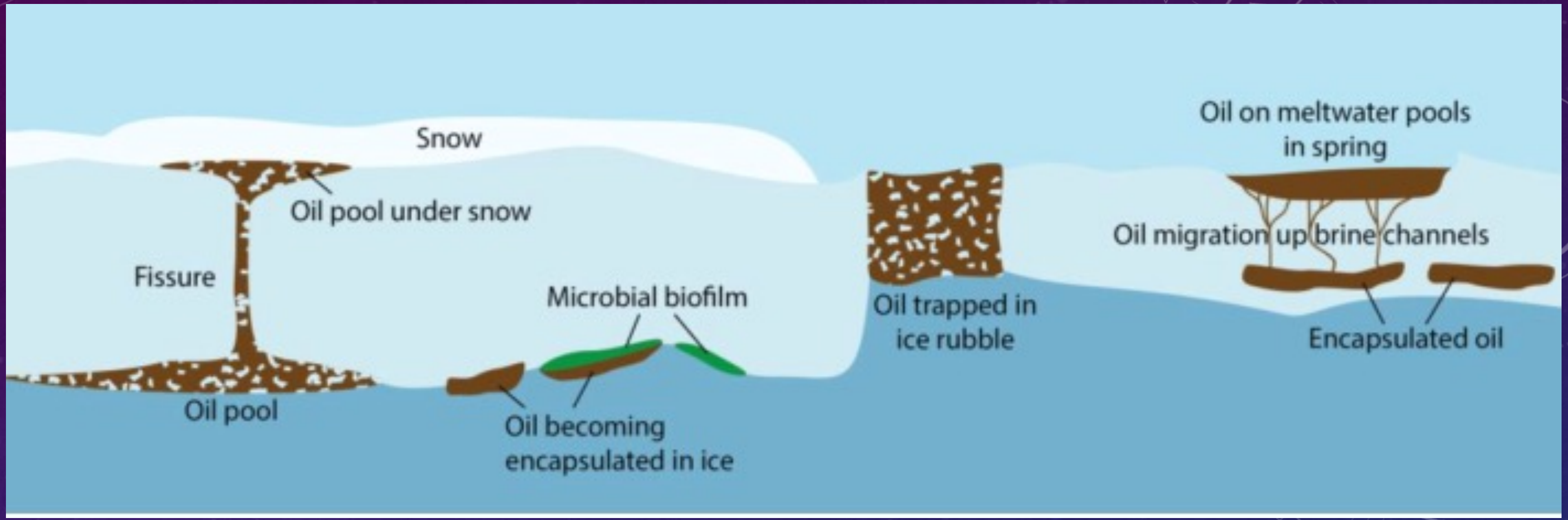
Most vulnerable are low energy layered beaches. Mudflats have high biota losses but faster recovery because of low retention, high abiotic rates





Abou-Khalil et al. 2022

OIL IN ICE



Taken from Royal Society of Canada, The Behaviour and Environmental Impacts of Crude Oil Released into Aqueous Environments (2015),

- Less weathering because limited gas exchange, low temperature, loss of wave energy
- Oil gradually floats up through ice
- Degradation in ice primarily in brine channels
- Low rates in mature ice (salts rejected) -5C or below, essentially zero below -20C

BIODEGRADATION

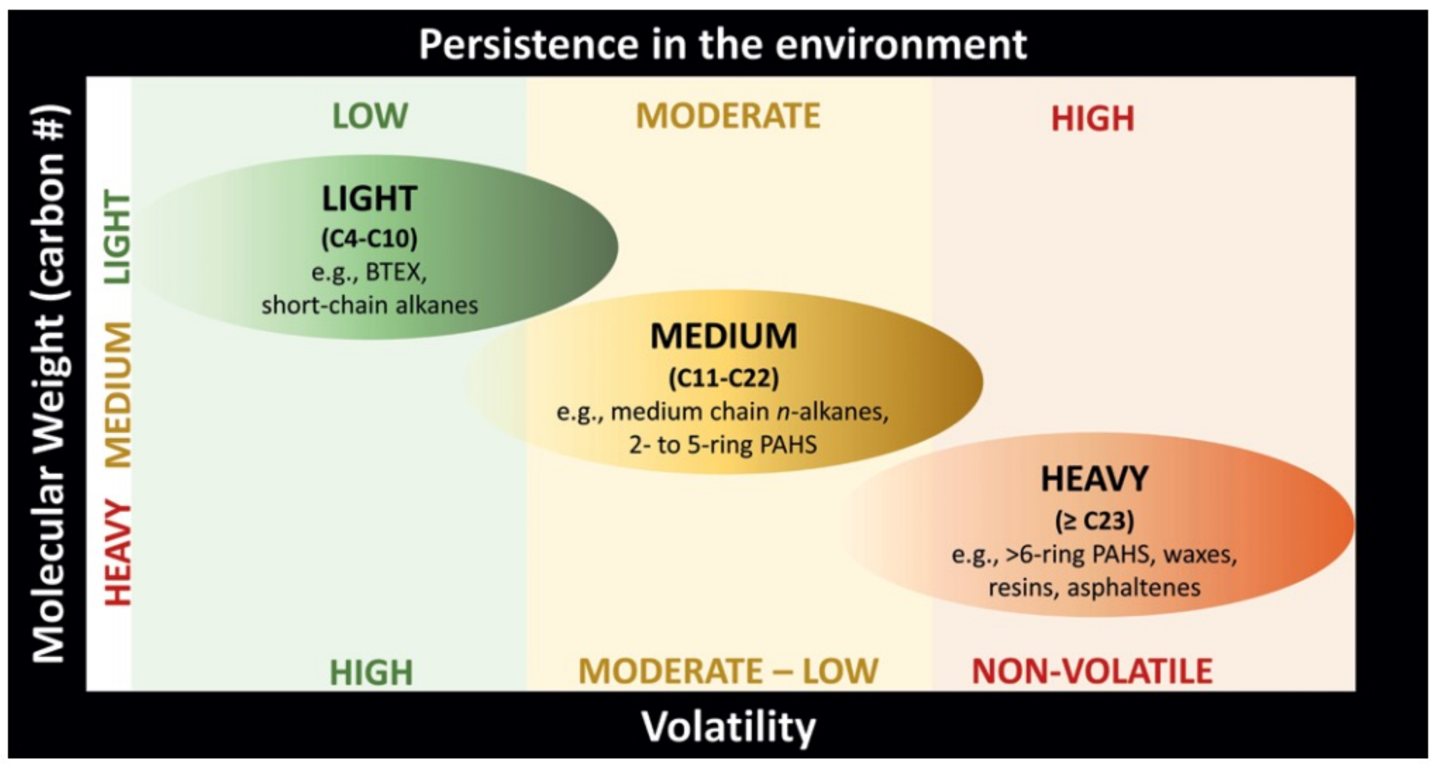
- Chemical Family/Molecular Weight
- Redox Conditions
- Available Surface Area
- Nutrient Availability
- Salinity
- Temperature
- Energy environment (wave action)

BIODEGRADATION OVERVIEW

- Natural attenuation of oil is robustly demonstrated in laboratory and real world studies in every studied aquatic environment for nearly every hydrocarbon
- As demonstrated by genomics tools, the agents are diverse ad hoc successional consortia of obligate hydrocarbon consuming bacteria, archaea and fungi
- The question is not whether it will degrade, but rather how fast
- Absent significant inhibiting factors, substantially complete degradation of aqueous oil occurs on an hours/days/weeks timescale

CHEMICAL FAMILY/MOLECULAR WEIGHT

- Light alkanes through to heavy PAHs, succession of degrader consortia

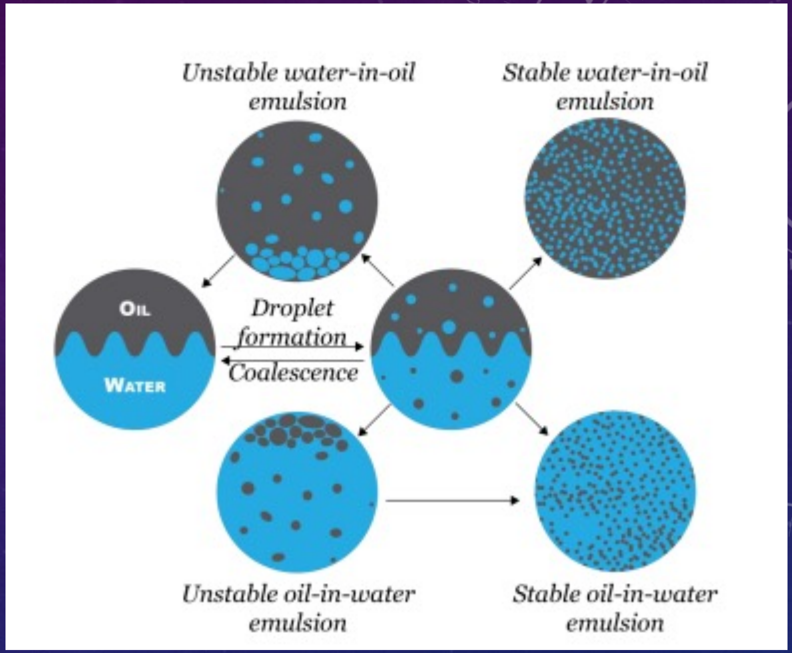


From National Academies of Sciences, Oil in the Sea IV: Inputs, Fates, and Effects (2022)

REDOX CONDITIONS

- Much faster in the presence of oxygen
- Alternate electron acceptors substantially slow the process

AVAILABLE SURFACE AREA



Taken from Royal Society of Canada, The Behaviour and Environmental Impacts of Crude Oil Released into Aqueous Environments (2015),

- Increasing surface area:
  - Increases area available for biofilms
  - Speeds transfer of sparingly soluble compounds into the aqueous phase
  - Adds to area for gas exchange and removal of metabolic products

NUTRIENT AVAILABILITY

- Perhaps surprisingly, does not limit biodegradation rates in most circumstances in water
- Much more relevant for stranded oil

SALINITY

- Salinity has to be well outside normal range to have material effect on degradation rates
- High salinity in the supra-tidal zone does slow it
- Literature does not compare rates in hyposaline vs saline environments

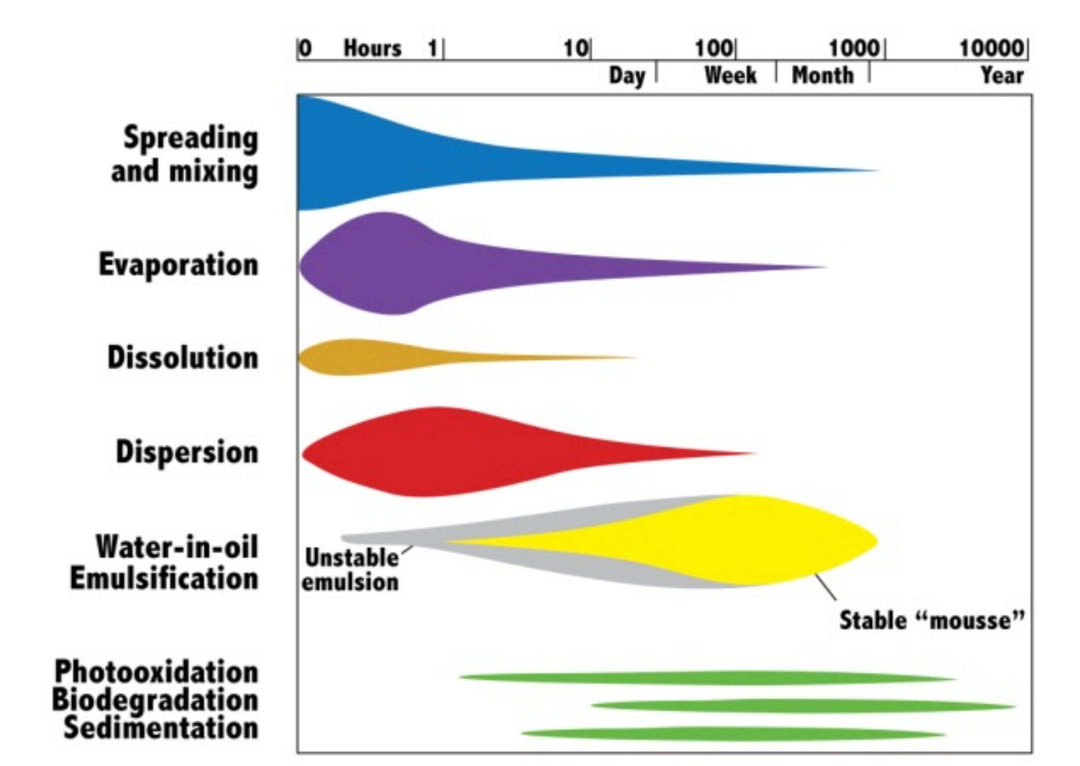
TEMPERATURE

- Surprisingly resilient to temperature until temperatures approach -5C
- Just different consortia membership

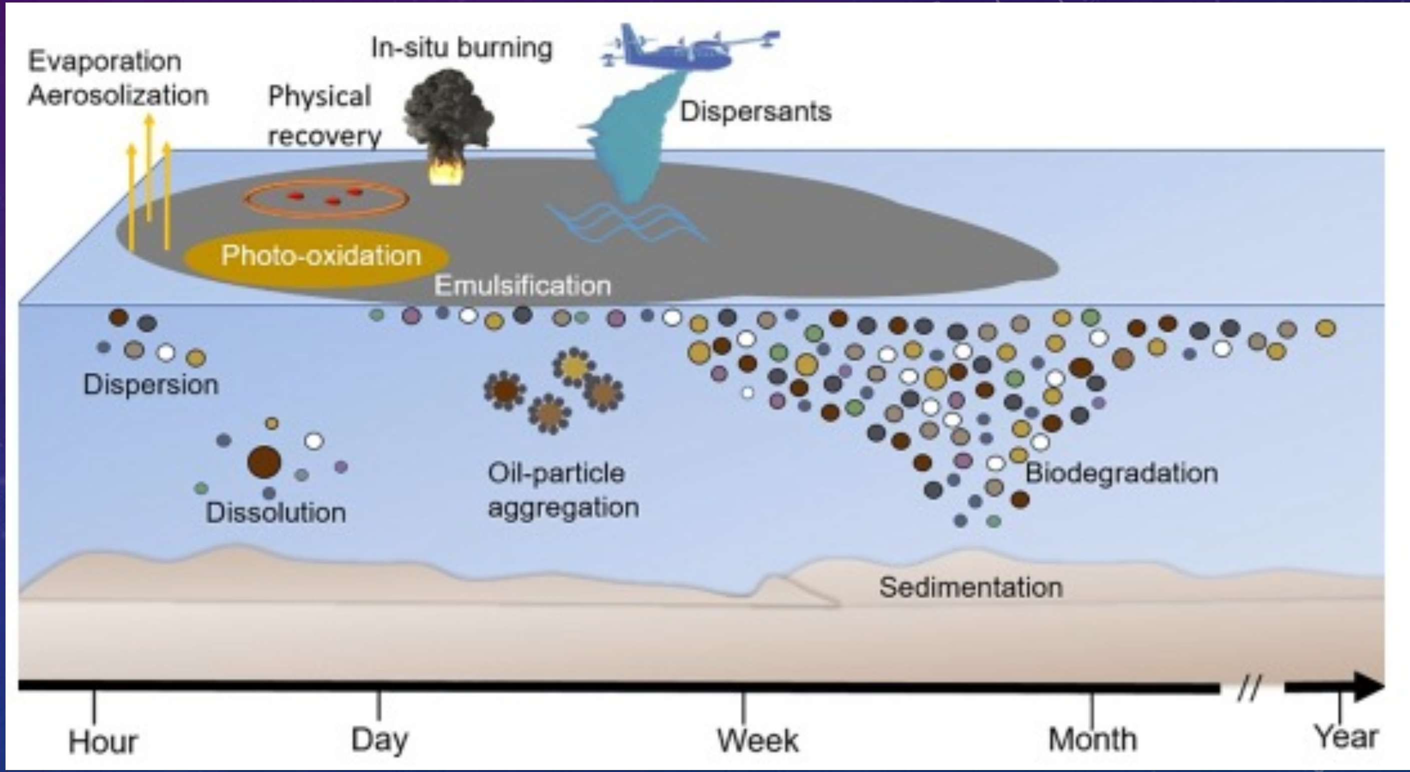
ENERGY ENVIRONMENT

- Increases surface area
- Increases emulsification
- Mixing

RELATIVE MAGNITUDE OF PROCESSES OVER TIME



Taken from Royal Society of Canada, The Behaviour and Environmental Impacts of Crude Oil Released into Aqueous Environments (2015),



Pequin et al. 2022

SPILL RESPONSE

- Physical intervention:
  - Removal from surface water
  - Removal from shorelines
- Chemical treatment
  - Dispersants
  - Surface washing agents
- In situ burning
- Enhanced bioremediation
  - Biostimulation
  - Bioaugmentation

From: https://wcmrc.com/preparedness/canadian-spill-response-regime/

REMOVAL

- Booms, skimmers, absorbents, pumps
- Passive or towed
- Struggles with emulsified oils

From: https://wcmrc.com/

From: https://www.vancouverislandfreedaily.com/news/port-alberni-marine-clean-team-learns-the-spill-drill/

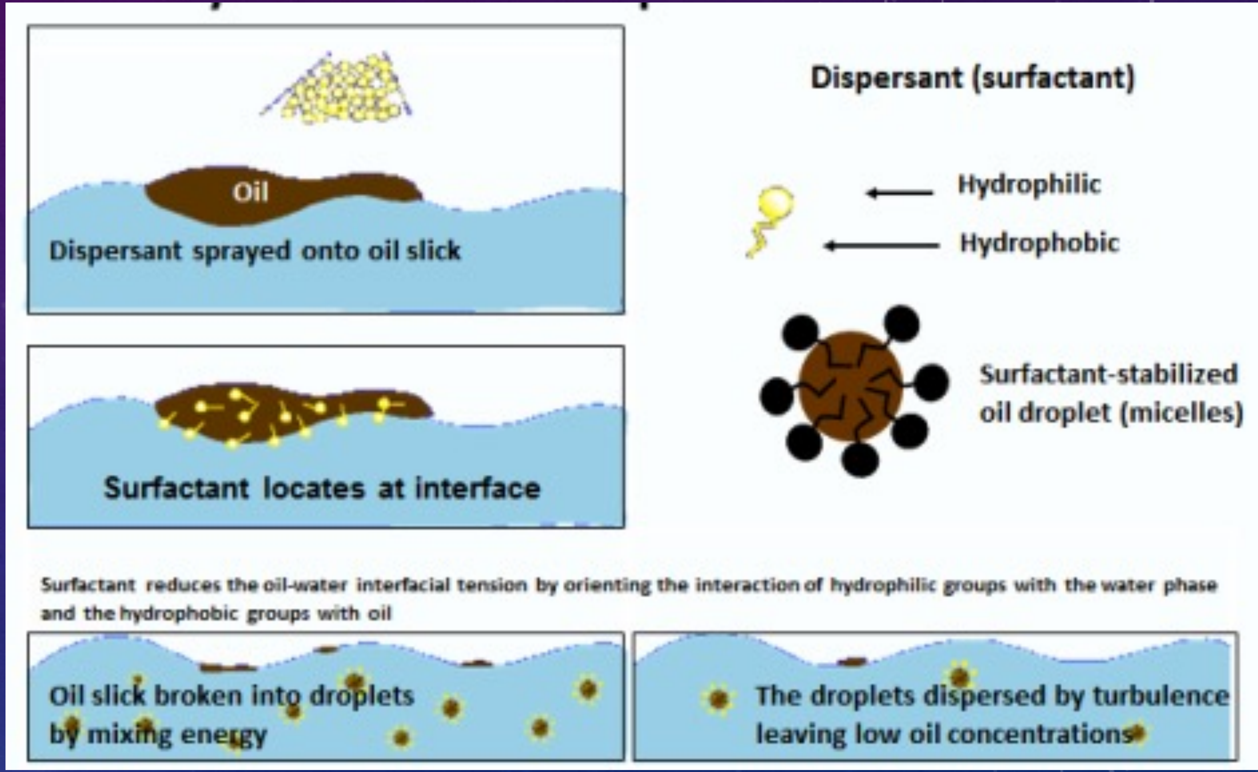
SHORELINE REMOVAL

- In-situ or ex-situ washing or removal/disposal – limited use except high traffic
- Tilling or raking to disrupt aggregations
- Absorbents
- Very high ecological impact (habitat disruption)
- NEBA is a highly used tool here
- Evidence of effects on responders will likely to limit this method

From: https://wcmrc.com/

CHEMICAL TREATMENT

- Dispersants to make the oil more soluble/more likely to disperse – light aliphatics with surfactants
  - Impact is not always clear
- Biosurfactants now being assessed, but there is already a huge mass of biosurfactants in seawater
- Surface washing – niche approach



Taken from Royal Society of Canada, The Behaviour and Environmental Impacts of Crude Oil Released into Aqueous Environments (2015),

IN SITU BURNING

- Generally only applicable to fresh spills
- Highly weather dependent
- Can remove up to 90% in ideal circumstances
- Residues often sink
- Herding agents can support this approach (not allowed in Canada)

From National Academies of Sciences, Oil in the Sea IV: Inputs, Fates, and Effects (2022)

BIOREMEDIATION

- Biostimulation with fertilizer demonstrated effectiveness in beach fouling, not applicable in open water
- Bioaugmentation (adding an inoculum) has not been demonstrated to be effective

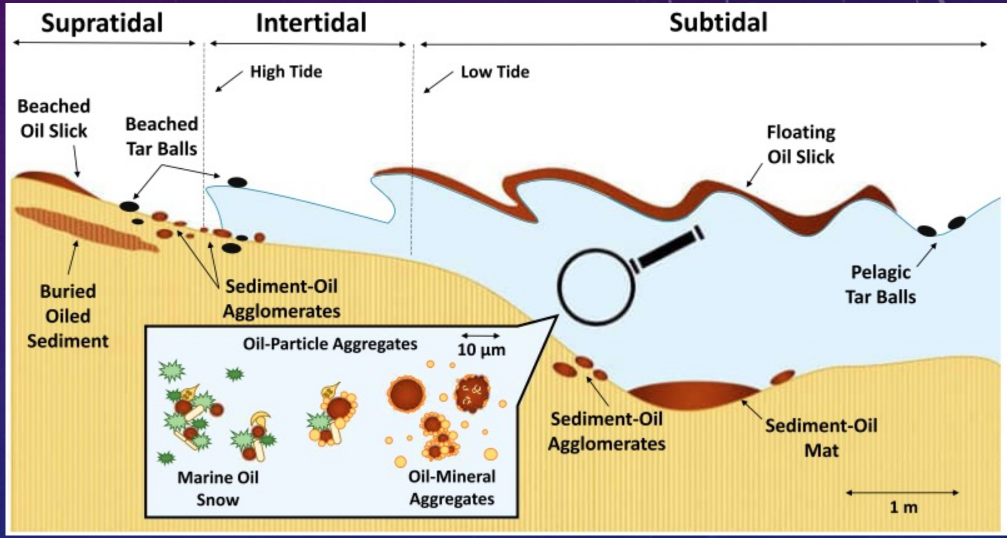
DECISION MAKING SUPPORT

- Experience
  - Sea Rose 2018
  - Nathan Stewart 2016
  - Arrow 1970
  - Exxon Valdez 1989
  - Sea Empress 1996
  - Prestige 2002
  - Deepwater Horizon 2010
  - Kalamazoo 2010
  - Wabamun Lake 2005

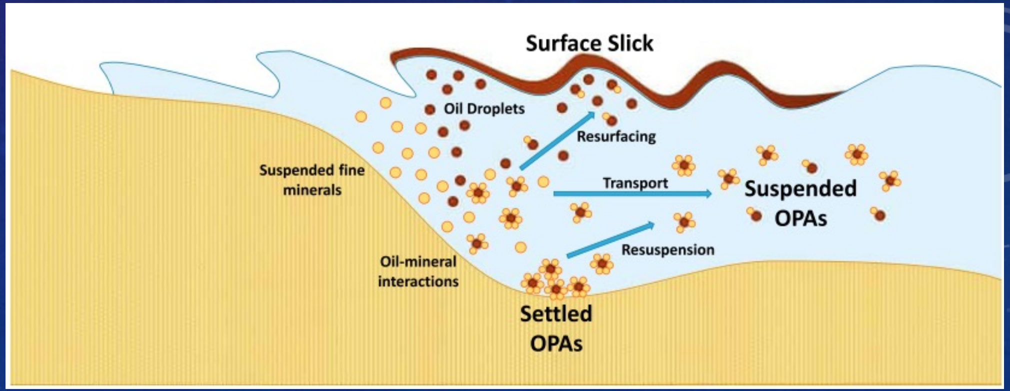
From: https://calgaryherald.com/business/energy/searose-fpso-vessel-allowed-to-return-to-work-on-offshore-oilfield-for-husky

DECISION SUPPORT MODELS

- Marine Oil Snow
- Quigg et al.
- Geng et al.
- Shoreline Response Model
- Oil Particle Aggregate



Oil residue size and locations found in nearshore environments (Gustitus & Clement, 2017)



OPA formation nearshore (Gustitus & Clement, 2017)

LITERATURE WEAKNESSES

- Much less data in ice environments
- Ecological effects of sunken oil
- Herding agents in Canadian Waters
- Usefulness of biosurfactants
- Fate and long term effects of asphaltenes and resins (C45+)
- Brackish environments
- Impact of diurnal migration of pelagic producers

SYNTHESIS

- Factors affecting spill response:
  - Duration – expected natural attenuation, risk of stranding
  - “Value” of receiving environment
  - Resiliency
  - Size of spill relative to ecosystems
  - Toxicity
  - Damage from spill response

ACKNOWLEDGEMENTS

- Fisheries and Oceans Canada for commissioning the underlying literature review
- Mike Shum, Leslie Beckmann, Chelsea Thorne and Michelle Ashley (fellow reviewers)