# Oil Behaviour in Freshwater Environments: Weathering and Incorporation into Models

Merv Fingas

Environment Canada

# Overview

- Behaviour in Fresh vs. Salt
- Evaporation
- Emulsification
- Natural Dispersion
- Dissolution
- Others


EXXON VALDEZ

# Fresh vs. Salt

- Most studies carried out on salt water
- …..despite fact that most spills occur in the freshwater environment
- --- but, freshwater spills aren't that spectacular and don't attract CNN
- There are some differences – but not completely different behaviours

# Behaviour of Oil

- Evaporation is the single-most important component
- Emulsification is the second most important
- Natural Dispersion
- Dissolution
- Photooxidation
- Sedimentation/interaction with particles
- Biodegradation

# Evaporation - Old Approach

- Presumed that oil evaporated like water
- Equations included wind speed, area (thickness), scale size, vapour pressure, inverse temperature, etc. etc.
- None of this information is available at a spill
- Further that evaporation should not be inverse of temperature!

# New Studies

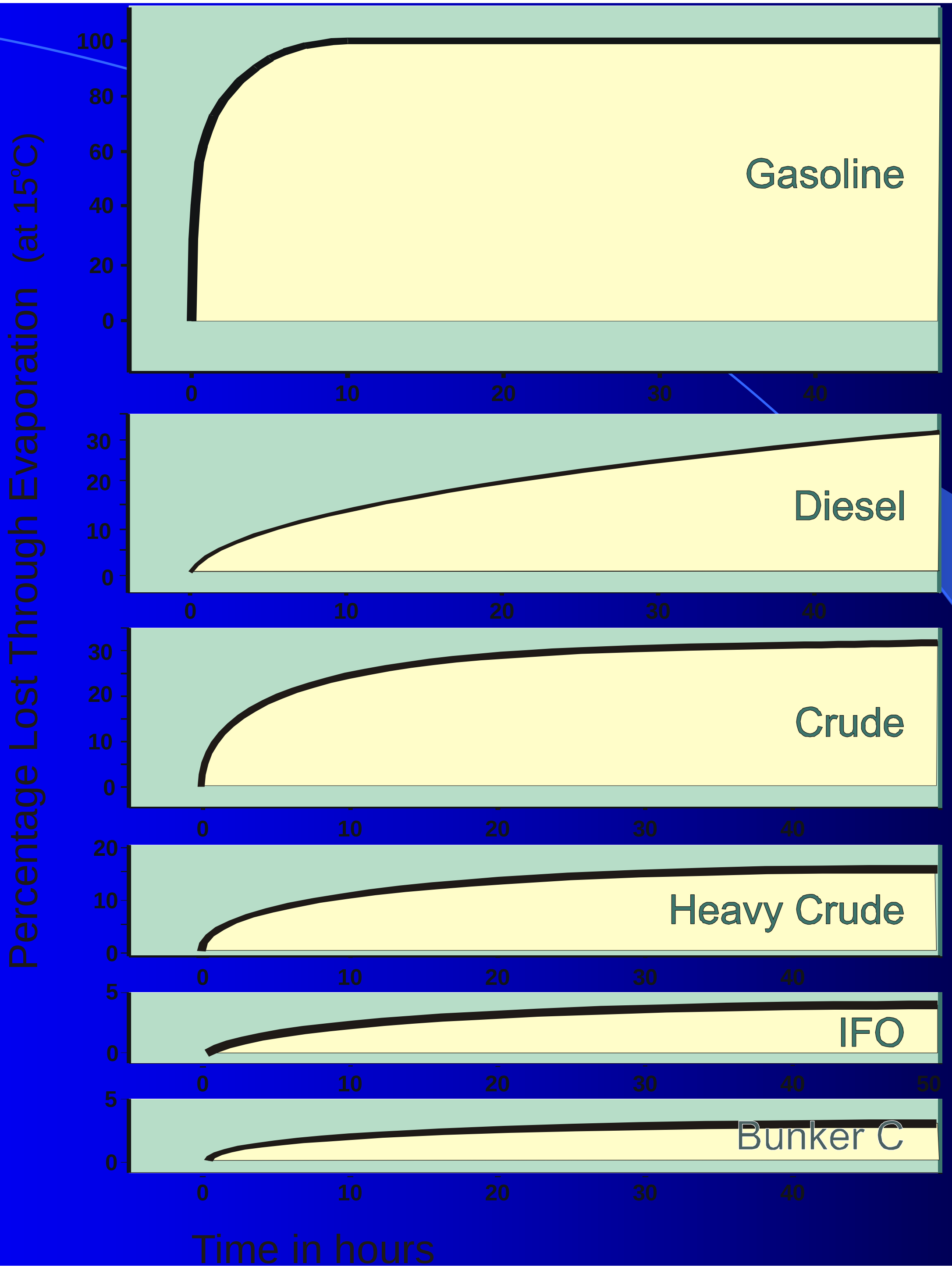
- Showed that oil evaporation was not air boundary-layer regulated like water
- Oil evaporation does not increase with area, inversely with thickness, but increases with volume
- Also found that a new simplified equation could be used

# Findings

- Studies showed that evaporation rate largely governed by temperature and time
- Evaporation could be described by simple equation such as: Evap = a*ln(t)

  Where a= constant

  t= time
- On short term basis some oils, eg. diesel fuel, are best modelled using square root of time


Percentage Lost Through Evaporation (at 15°C)
Time in hours
Gasoline
100
80
60
40
20
0
0
10
20
30
40
Diesel
30
20
10
0
0
10
20
30
40
Crude
30
20
10
0
0
10
20
30
40
Heavy Crude
20
10
0
0
10
20
30
40
IFO
5
0
0
10
20
30
40
50
Bunker C
5
0
0
10
20
30
40

# Distillation Data

- **Is readily available because refineries need it**
- **For many crudes is similar and has similar slopes**
- **Gasoline and bunkers have different slopes and curve characteristics**
- **Diesel and similar products have a very narrow boiling range**

# Prediction Using Distillation

- Combining with temperature correlations:
  $\text{Evap}\% = [0.165(\%D) + 0.45(T-15)]*\ln(t)$
  Where: %D = percentage distilled at 180 C
  T = temperature, Celsius
  t = time in minutes

# Empirical Equations

- Have been developed for over 250 oils and products
- Are also available on web site www.etc-cte.ec.gc.ca/
- EC Continue to measure these

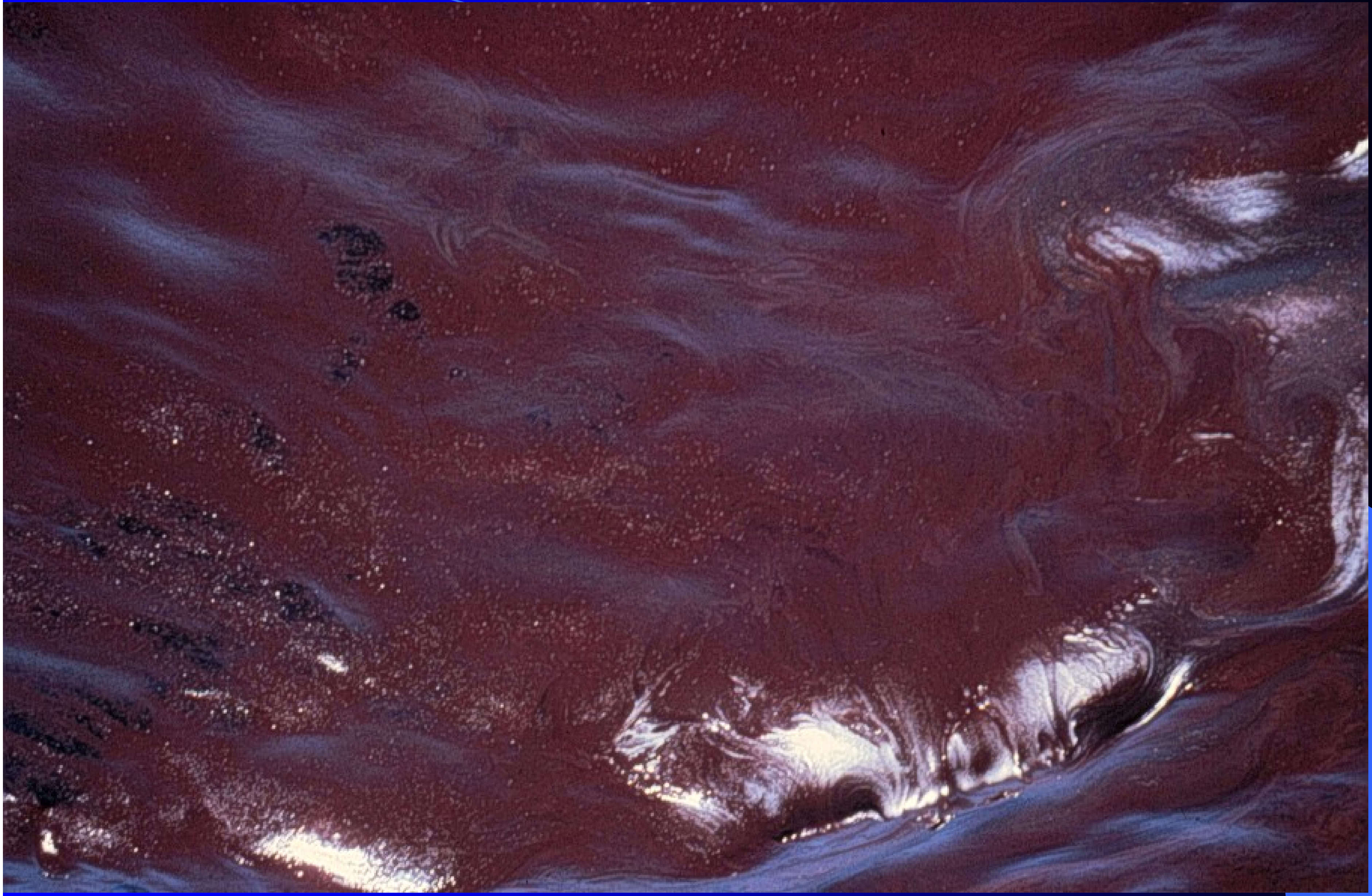
| **Oil Type** | **Equation** | **Oil Type** | **Equation** |
|---|---|---|---|
| Adgo | $\%Ev = (.11 + .013T)\sqrt{t}$ | Jet Fuel (Anch) short term | $\%Ev = (1.06 + .013T)\sqrt{t}$ |
| Adgo - long term | $\%Ev = (.68 + .045T)\ln(t)$ | Komineft | $\%Ev = (2.73 + .045T)\ln(t)$ |
| Alaska North Slope (2002) | $\%Ev = (2.86 + .045T)\ln(t)$ | Lago | $\%Ev = (1.13 + .045T)\ln(t)$ |
| Alberta Sweet Mixed Blend | $\%Ev = (3.24 + .054T)\ln(t)$ | Lago Treco | $\%Ev = (1.12 + .045T)\ln(t)$ |
| Amauligak | $\%Ev = (1.63 + .045T)\ln(t)$ | Lucula | $\%Ev = (2.17 + .045T)\ln(t)$ |
| Amauligak - f24 | $\%Ev = (1.91 + .045T)\ln(t)$ | Main Pass Block 306 | $\%Ev = (2.86 + .045T)\ln(t)$ |
| Arabian Medium | $\%Ev = (1.89 + .045T)\ln(t)$ | Main Pass Block 37 | $\%Ev = (3.04 + .045T)\ln(t)$ |
| Arabian Heavy | $\%Ev = (1.31 + .045T)\ln(t)$ | Malongo | $\%Ev = (1.67 + .045T)\ln(t)$ |
| Arabian Heavy | $\%Ev = (2.71 + .045T)\ln(t)$ | Marinus Turbine Oil | $\%Ev = (-0.68 + .045T)\ln(t)$ |
| Arabian Light | $\%Ev = (2.52 + .037T)\ln(t)$ | Marinus Valve Oil | $\%Ev = (-0.68 + .045T)\ln(t)$ |
| Arabian Light | $\%Ev = (3.41 + .045T)\ln(t)$ | Mars TLP | $\%Ev = (2.18 + .045T)\ln(t)$ |
| Arabian Light (2001) | $\%Ev = (2.4 + .045T)\ln(t)$ | Maui | $\%Ev = (-0.14 + .013T)\sqrt{t}$ |

# Emulsion Formation

- Not much understood until recently
- Old model equations are totally wrong
- Is somewhat complex and very oil composition dependent

# Overview of Stabilization

- There are two fundamental mechanisms by which oil retains water
  - (1) Viscosity – water cannot coalesce
  - (2) Surfactant action of asphaltenes and resins – chemical action

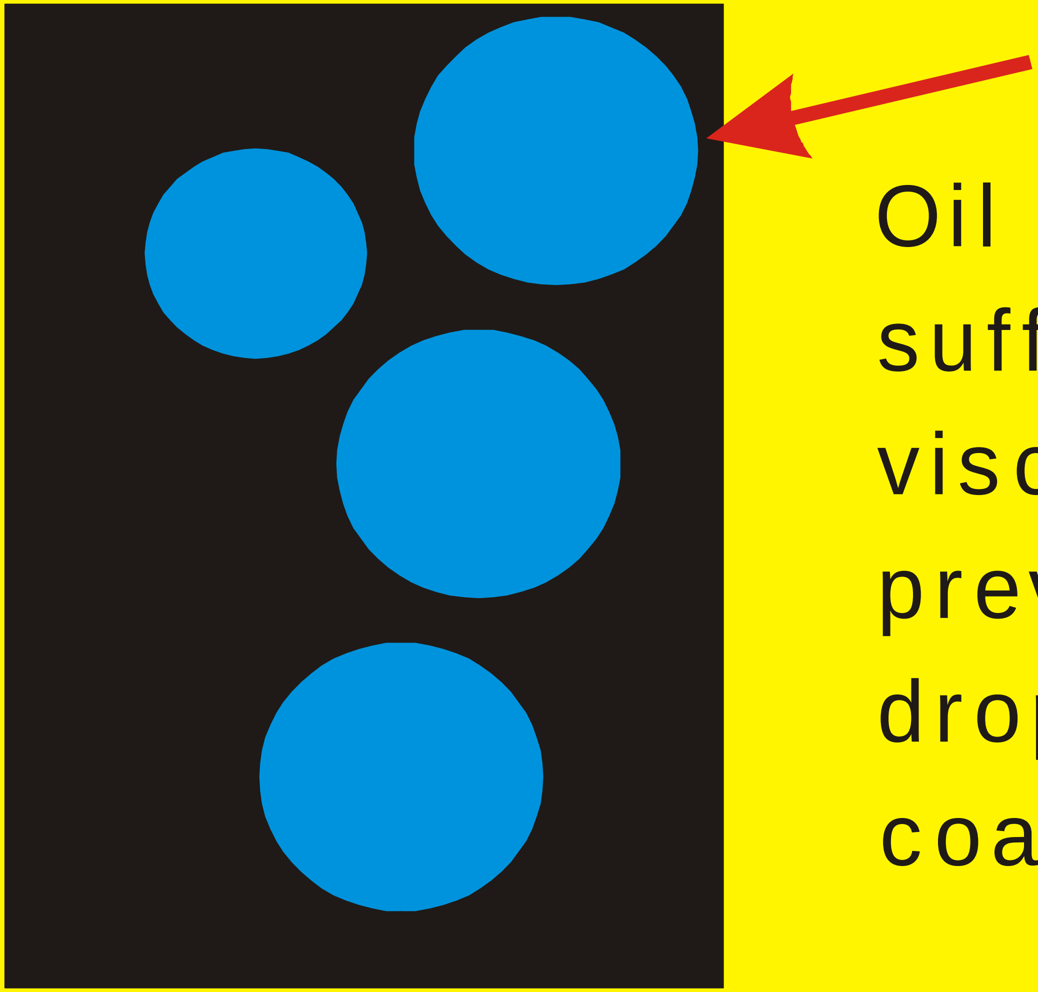


# Background

- Emulsions have been studied since 1968
- Information on how they are formed not clear until early 90’s
- Several workers now have many papers on formation mechanisms and stability
- Unfortunately – some of older, incorrect hypotheses still float around

# Stabilization Mechanisms

- Viscosity – if oil is viscous enough – water droplets injected cannot coalesce or sink through oil mass
- Correspondingly – too little viscosity, the droplets are not held, too much they cannot enter

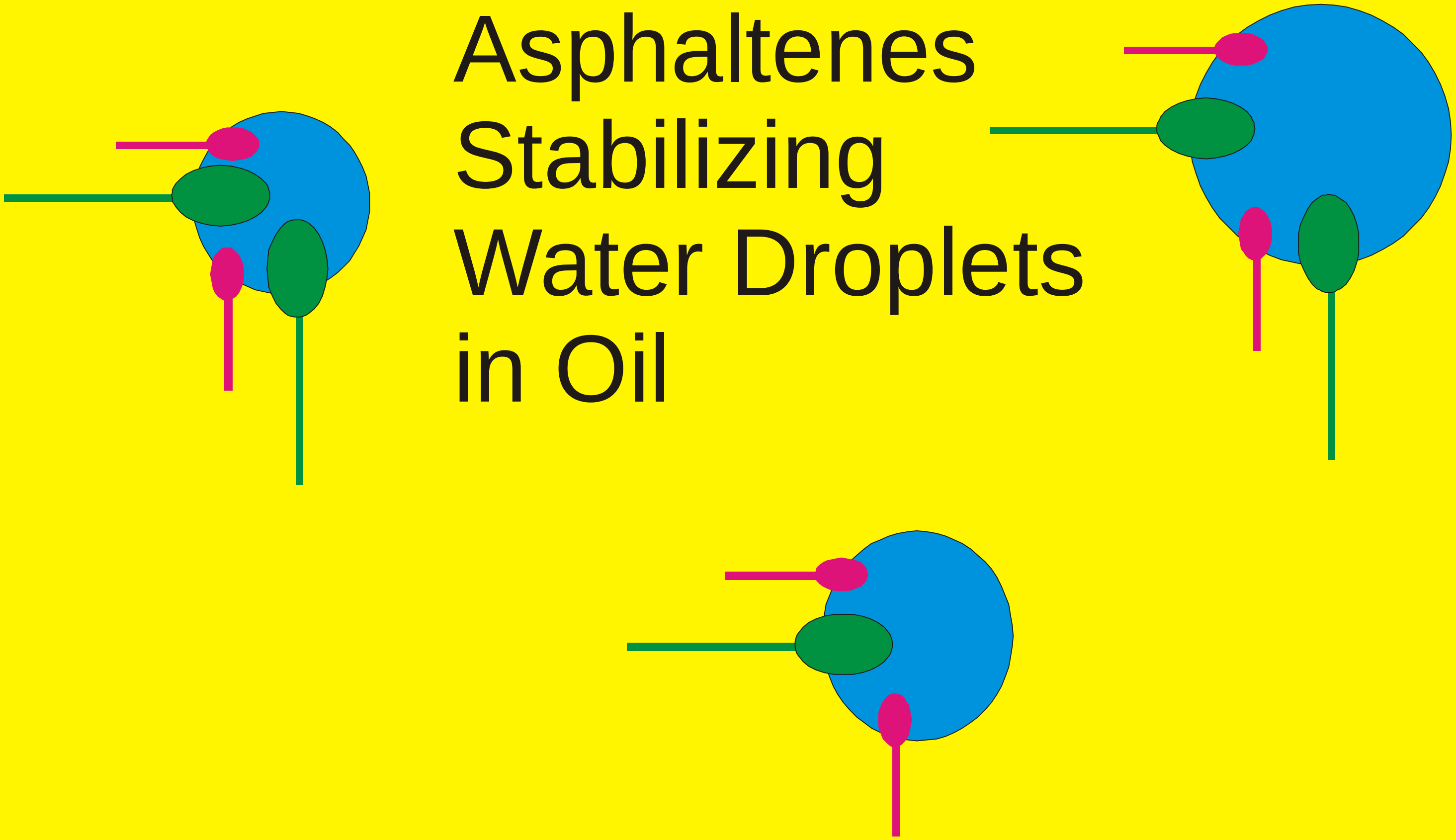


Oil layer is sufficiently viscous to prevent oil droplets from coalescing

# Surfactant Stabilization

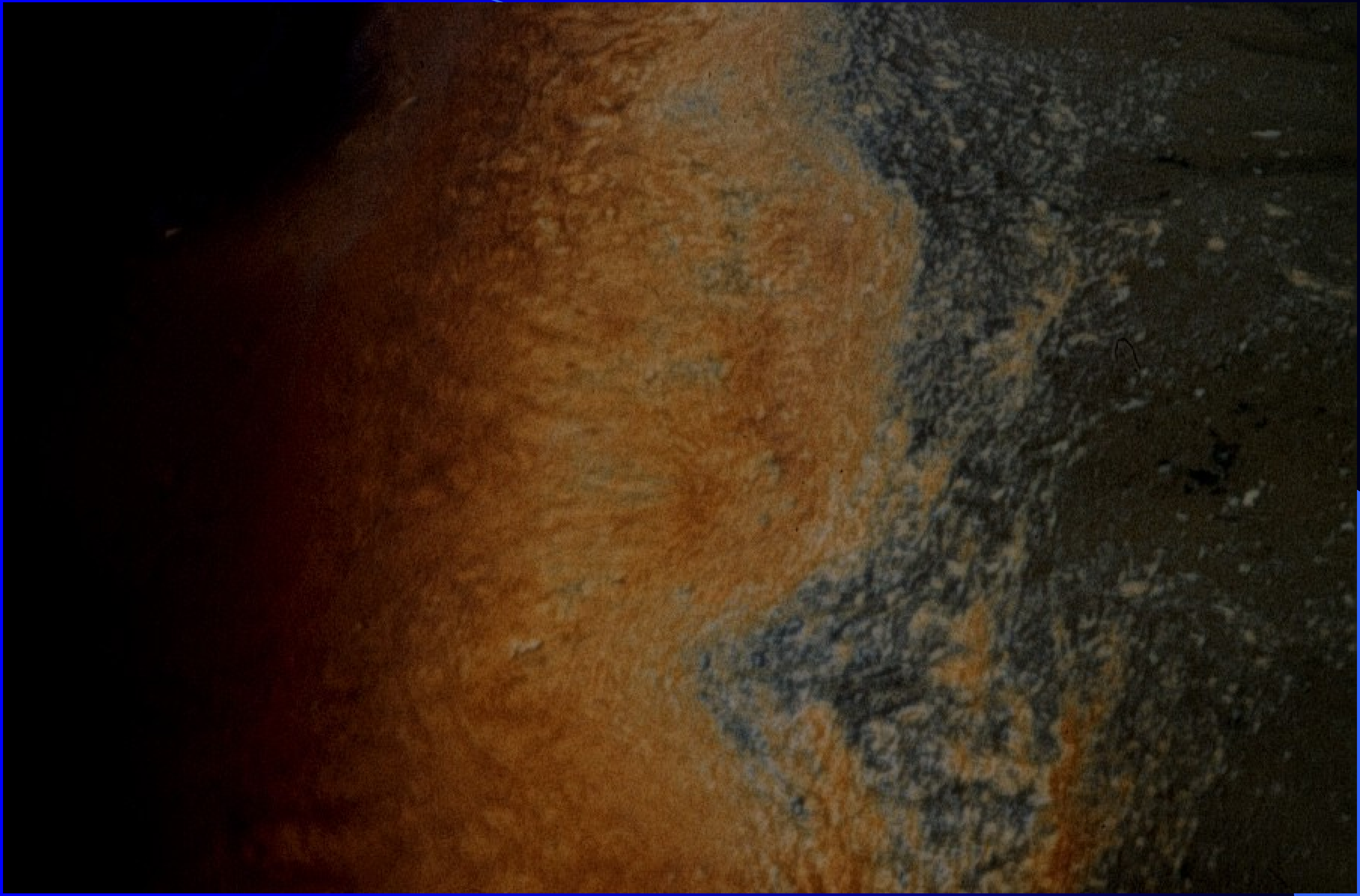
- Resins and asphaltenes act to stabilize water droplets in oil
- Polar constituents reside in the water and non-polar in the oil, thus locking up the droplet
- Asphaltenes form much more stable emulsions, but take a longer time to migrate to oil/water interface

# Resins and Asphaltenes Stabilizing Water Droplets in Oil



# Asphaltene and Resin Stabilization

- Is aided by viscosity – the water droplets need to be held in place long enough for the surfactants to migrate to the interface
- Asphaltene migration still continues after one month



# Water Content

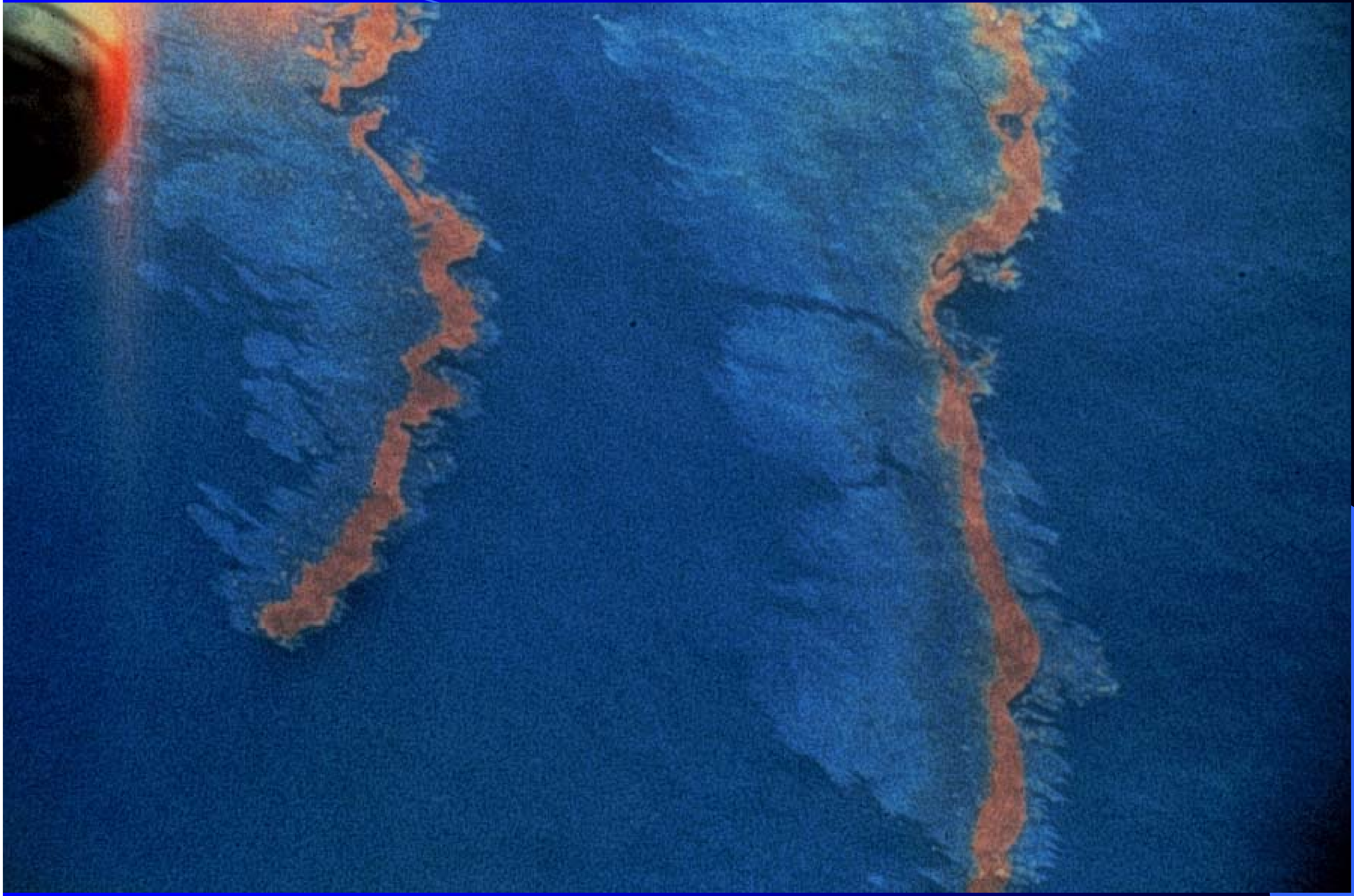
- Surfactant stabilized emulsions begin at about 70% - this is the maximum packing of one sphere size inside a space
- With some water loss this can drop to about 60%
- With some water particle size differences could be initially as high as 90%

# More on Water Content

- Emulsions therefore have about 60 to 90% water initially - typically 60 to 70% after a period of time
- Water content less than 60 % initially indicates viscosity entrainment of water with little stability – this is not an emulsion

# Types of Water-in-oil States

- Emulsions – two types – stable and meso-stable (defined by how long they last, electric and viscoelastic measurements)
- Entrained – simple viscosity-bound water in oil – lasts only minutes to a few hours
- Unstable – oil that simply doesn't hold water either way




27 13:45

# Studies of Various Types

- Over 200 oils were studied as to type of emulsion they form
- All forms were studied over periods as long as 1 year
- Some stable emulsions have been in lab for over 10 years!
- Studies of real emulsions confirm lab studies


6
6
5
4
4

# Windows for Formation

| | | Stable | Meso | Entrained | Unstable |
|---|---|---|---|---|---|
| **Density** | g/mL | 0.85-0.97 | 0.84-0.98 | 0.97-0.99 | 0.8-1.03 |
| **Viscosity** | (mPa.s) | 15-10000 | 6-23000 | 2000-60000 | 2 - 5.1 X $10^6$ |
| **Saturates** | % | 25-65 | 25-65 | 19-32 | 23-80 |
| **Aromatics** | % | 20-55 | 25-40 | 30-55 | 5-12 |
| **Resins** | % | 5-30 | 6-30 | 15-30 | 0-32 |
| **Asphaltenes** | % | 3-20 | 3-17 | 3-22 | 0-32 |
| **Asphaltenes/Resins** | | 0.74 | 0.47 | 0.62 | 0.45 |

# Old Myths

- waxes have a e
- all water-in-o states are e ulsions
- water conten an vary from 0 90
- all emulsions re the same
- water content relevant or a discrim ator
- RIP - hopef lly

# Terminology

- ‘Emulsion’ implies stability and therefore it should only be used for stable or meso-stable emulsions
- Entrained water states should be called that
- Very important to distinguish between types because countermeasures depends very much on stability

# Distinguishing

## Typical Properties for the Water-in-Oil States

| | | Stable | Meso | Entrained | Unstable |
|---|---|---|---|---|---|
| **Day of Formation Appearance** | | brown solid | brown viscous liquid | black with large droplets | like oil |
| **Water Content on first day** | % | 80 | 62 | 42 | 5 |
| **Appearance after one week** | | brown solid | broken, 2 or 3 phases | separated oil and water | like oil |
| **Water Content after week** | % | 79 | 38 | 15 | 2 |
| **Stable time** | days | >30 | <3 | <0.5 | not |
| **Properties on day of formation** | | | | | |
| **Average Ratio of Viscosity Increase** | | 1100 | 45 | 13 | 1 |
| **Properties after one Week** | | | | | |
| **Average Ratio of Viscosity Increase** | | 1500 | 30 | 2 | 1 |
| **Properties after one Year** | | | | | |
| **Average Ratio of Viscosity Increase** | | 1400 | 15 | 1 | 1 |

# Differences from Salt to Fresh

- Salt water produces more stable emulsions than fresh water
- Paper shows some numeric examples of differences
- Emulsification is not as frequent in fresh water environments – probably because of types spilled more frequently and energy differences

# Summary

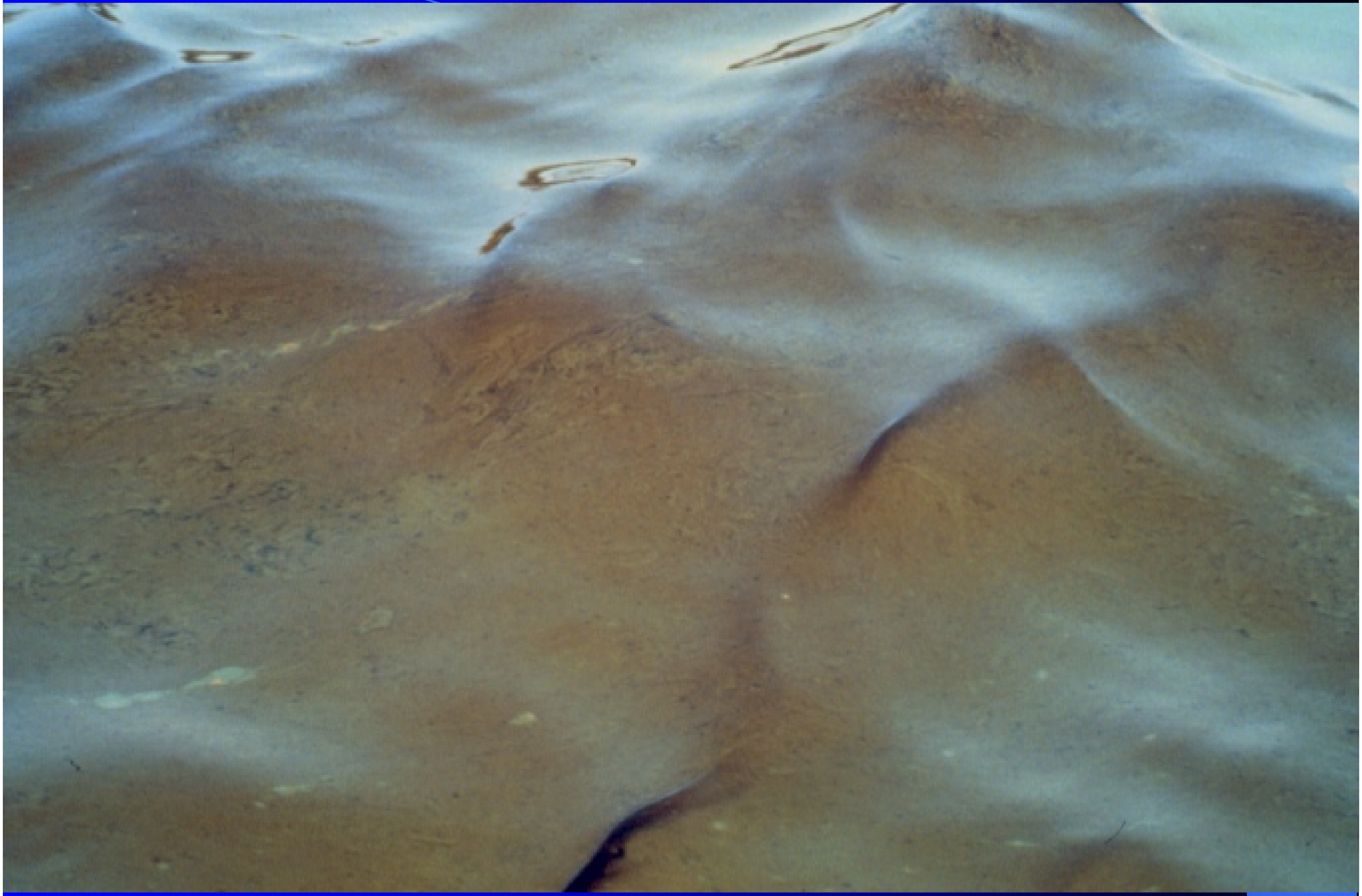
- Four water-in-oil states exist: stable and meso-stable emulsions, entrained and unstable
- The four states are easily distinguished by: colour, appearance, lifetime, rheological measures
- Each state has a ‘window’ of starting oil viscosity, density, asphaltene/resin content

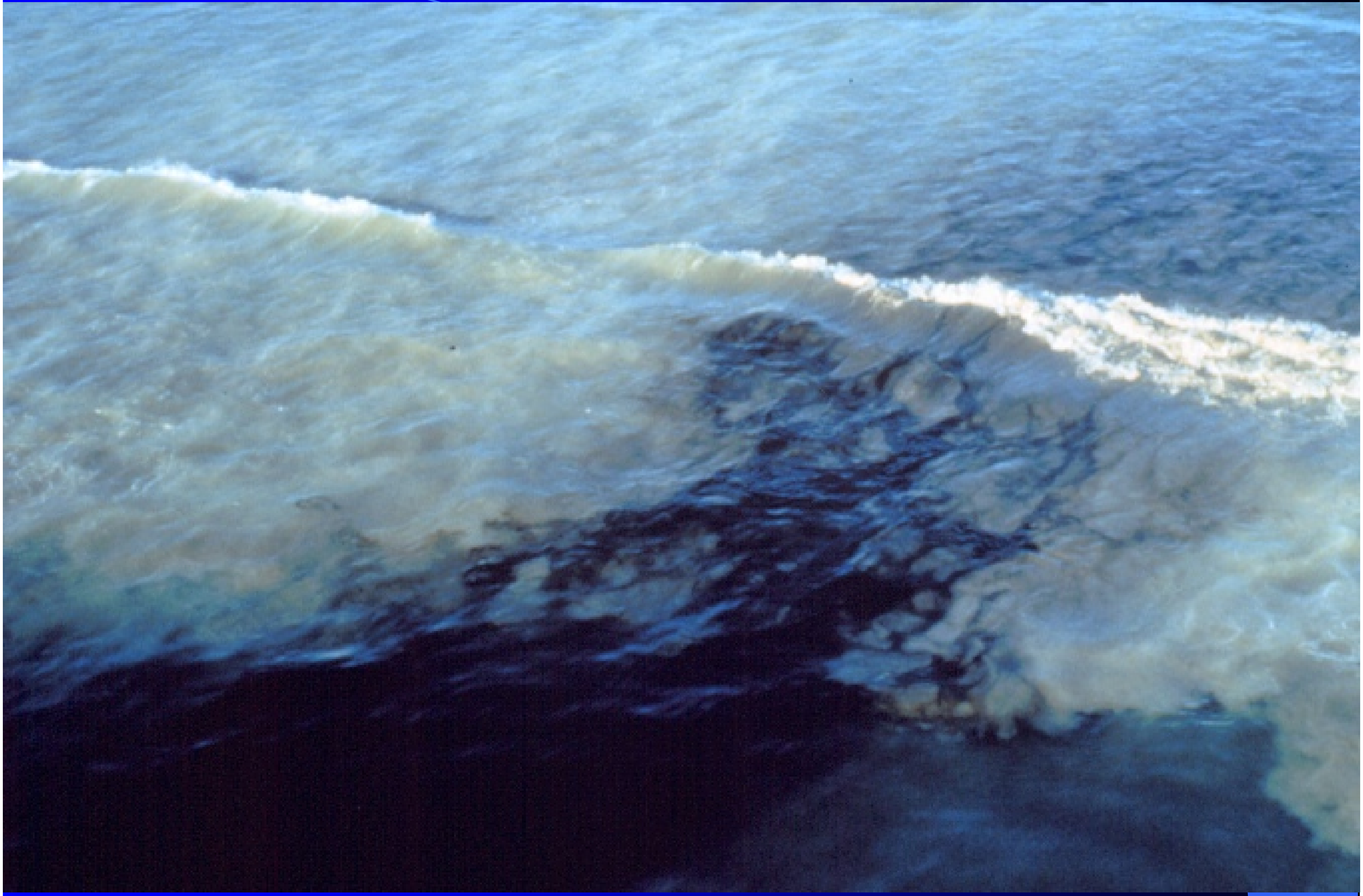
# Natural Dispersion

- Has been studied by Delvigne in Holland and algorithms developed
- These algorithms over-predict what goes into the water
- Much more research needed here
- Problem is measurement and accurate simulation

# Natural Dispersion

- Is known to be very significant with light oils in heavy seas – but in freshwater??
- Several spills large dispersed naturally: Braer off Scotland, Ecofisk Bravo blowout in Norway
- Several spills inland have dispersed somewhat in rapid rivers, over dams
- Heavier oils not subject





# Dissolution

- No good model
- Solubility of several oils measured
- Solubility of oils ranges from about 1 to 200 ppm – most crudes are in range of 2 to 40 ppm
- Needs more research

# Photooxidation

- Poorly understood at this time
- Are some old tid-bits of work – but may not be accurate
- Requires research

# Photooxidation

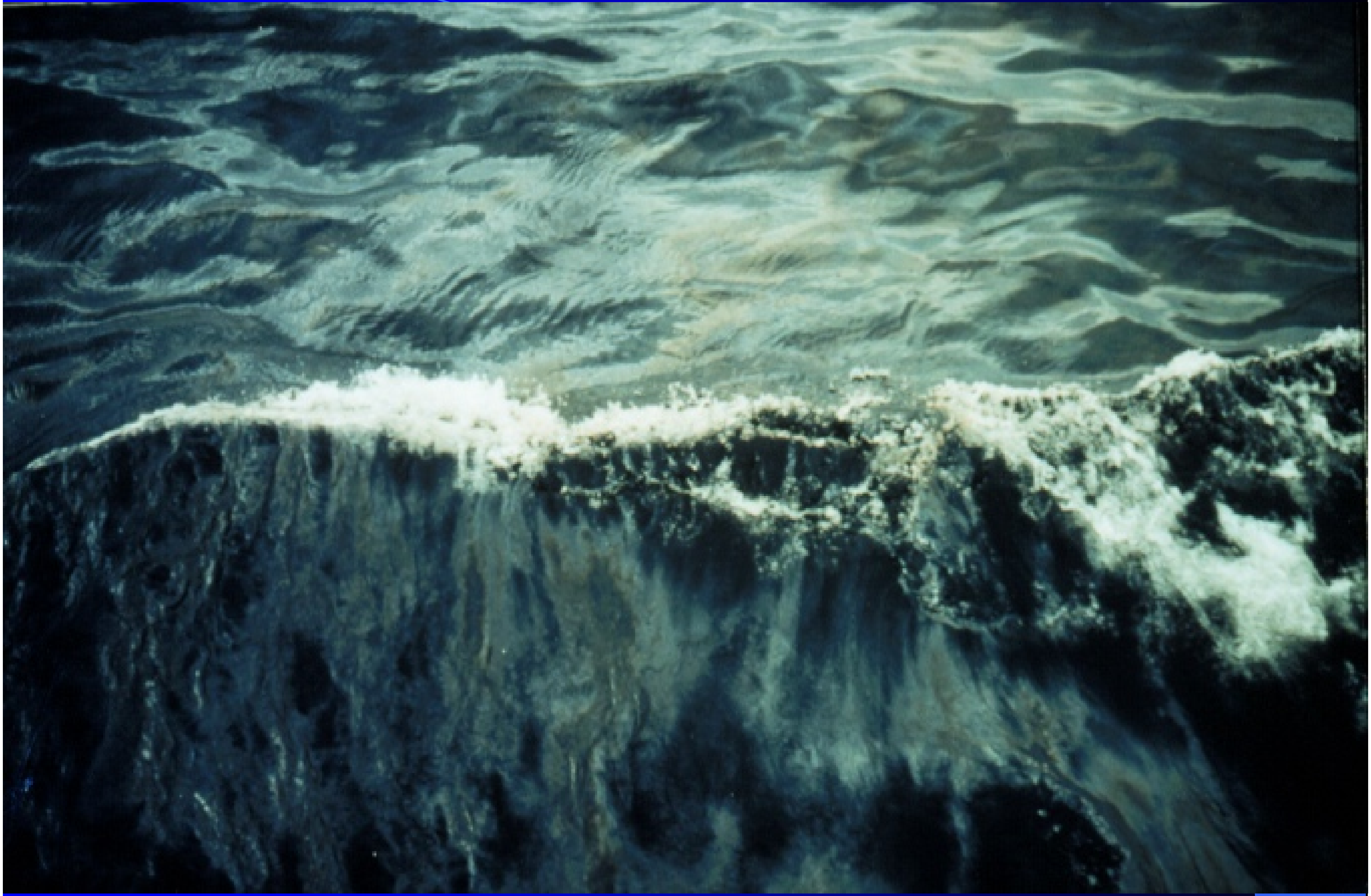
- What is known – does occur with some oils more than others – results in oxygenates which can promote emulsification – products may be more toxic than starting oil

# Sedimentation/Interaction with Particles

- Lot of activity lately – but little quantitative prediction work
- It is known in several spills that oil has often sedimented to a large degree (eg. Amoco Cadiz) – but no good quantitative data at this time
- Relation to freshwater somewhat studied

# Interaction with Particles

- Oil-fines interaction has been studied and field kits even available to examine the phenomena
- Oil-fines interaction can remove oil from a slick or even from a shoreline
- No quantitative prediction information available however
- Has been tested on Great Lakes



# Biodegradation

- Is a remover of diesel and light fractions
- Effect of biodegradation on old spills can be as little as 1 to 2%
- Asphalt and tar do not readily biodegrade
- Biodegradation competitive to evaporation – especially C12 to C18
- Long-weathered oil can even lose biomarkers to degradation

# Closing Remarks

- Behaviour and fate of oil is dominated by the composition – but also a function of the environment
- Differences between fresh and salt water environments are small – but in emulsification may be significant
- Some significant new work which can be incorporated into models