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

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)

$$\text{Where } a= \text{constant}$$
$$t= \text{time}$$

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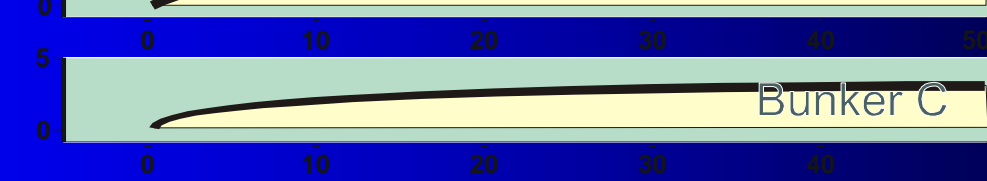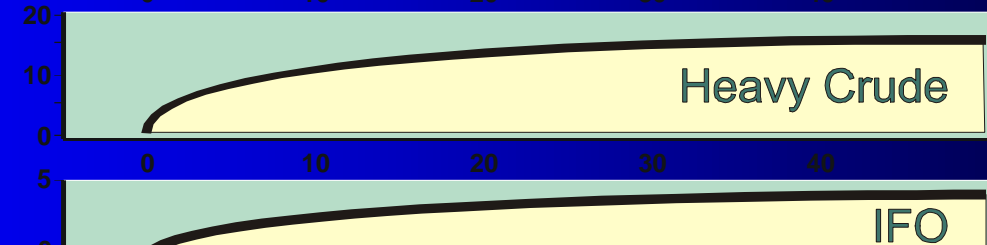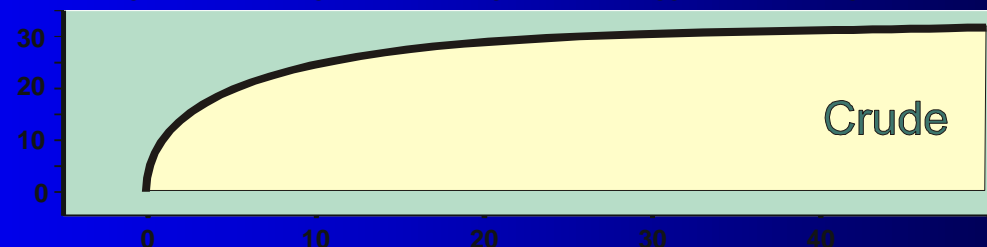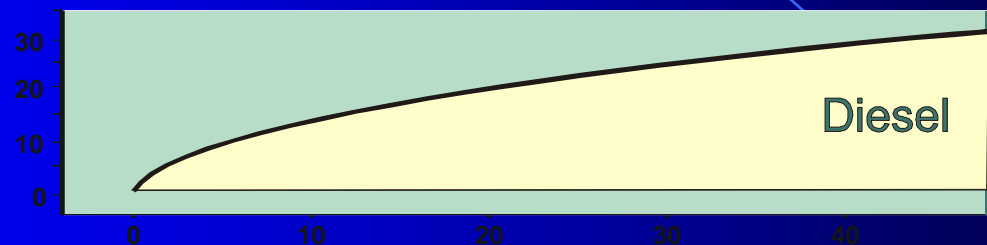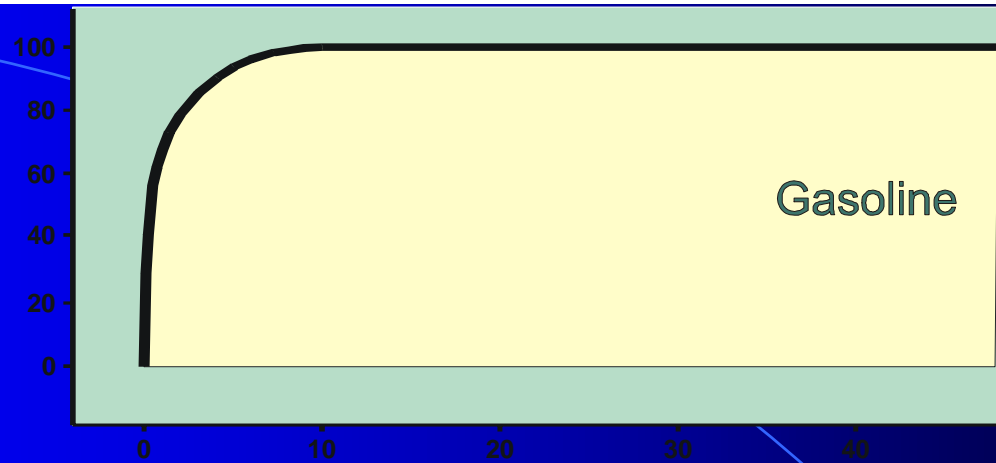
Distillation Data

- **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:
  $$Evap\% = [0.165(\%D) + 0.45(T\text{-}15)]*\ln(t)$$
  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
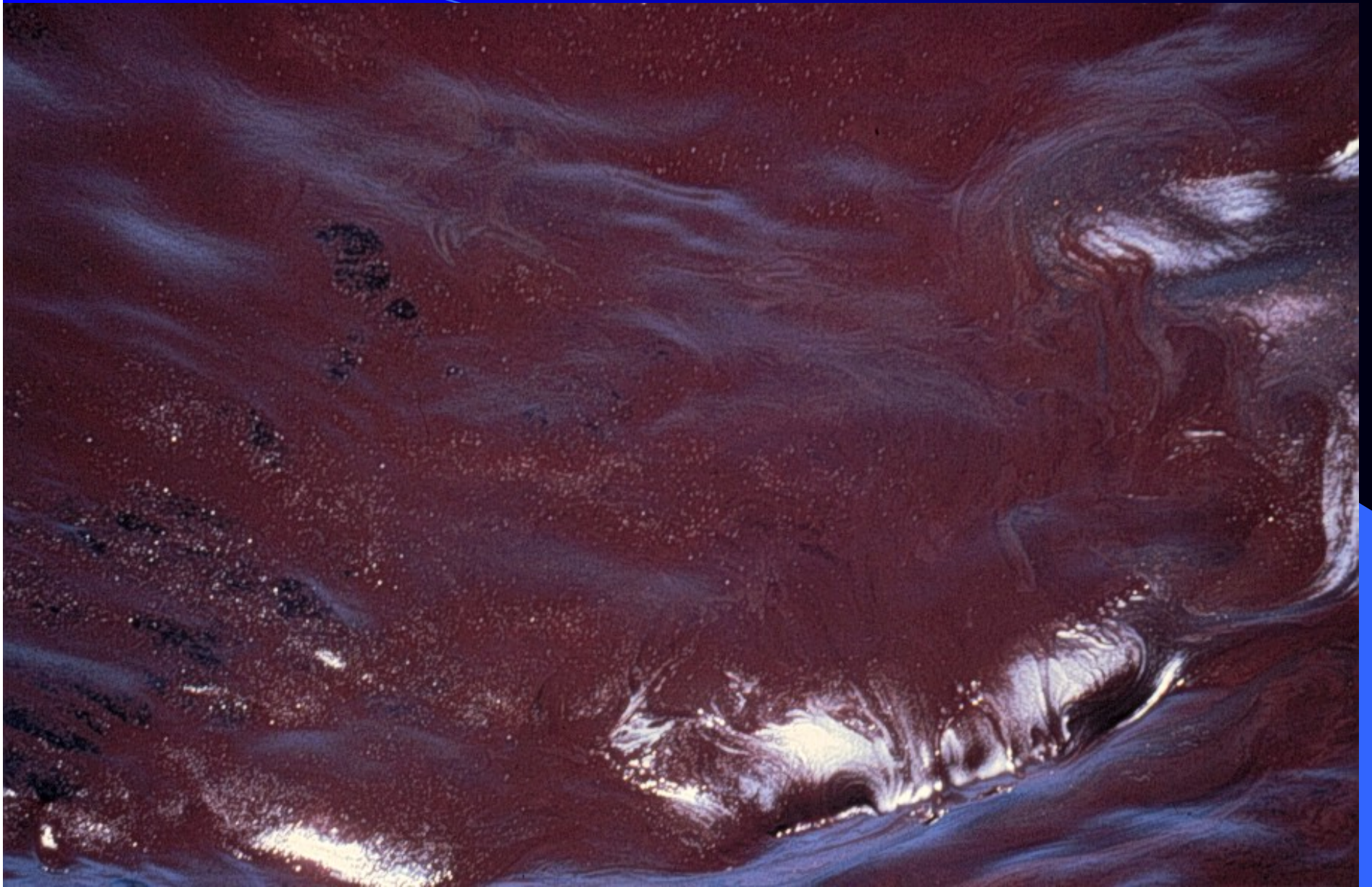
Background

- 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
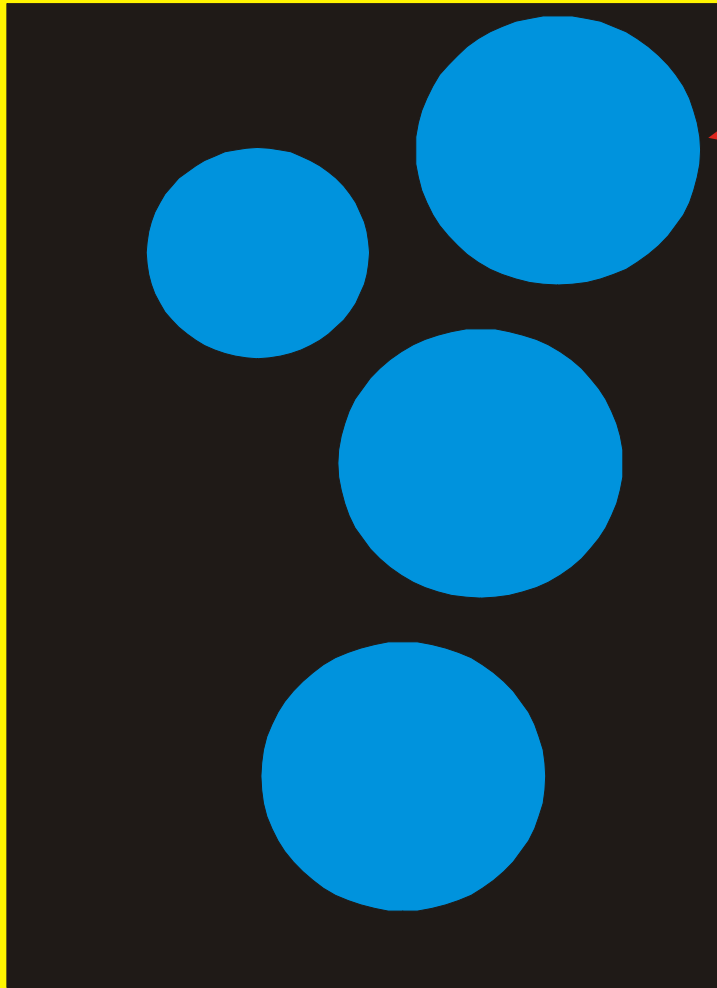
Oil layer is sufficiently viscous to prevent oil droplets from coalescing

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
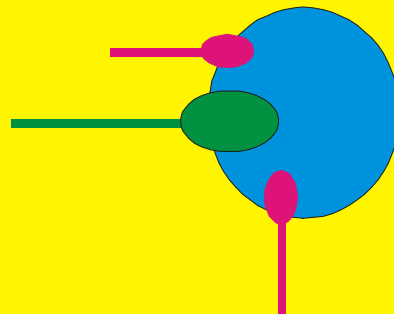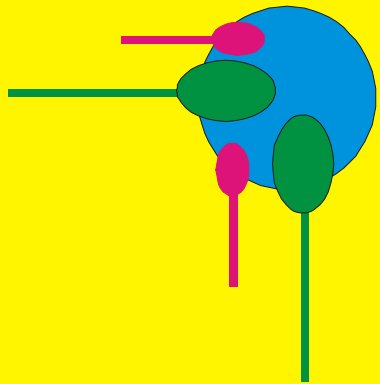
Asphaltene and Resin Stabilization

- 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
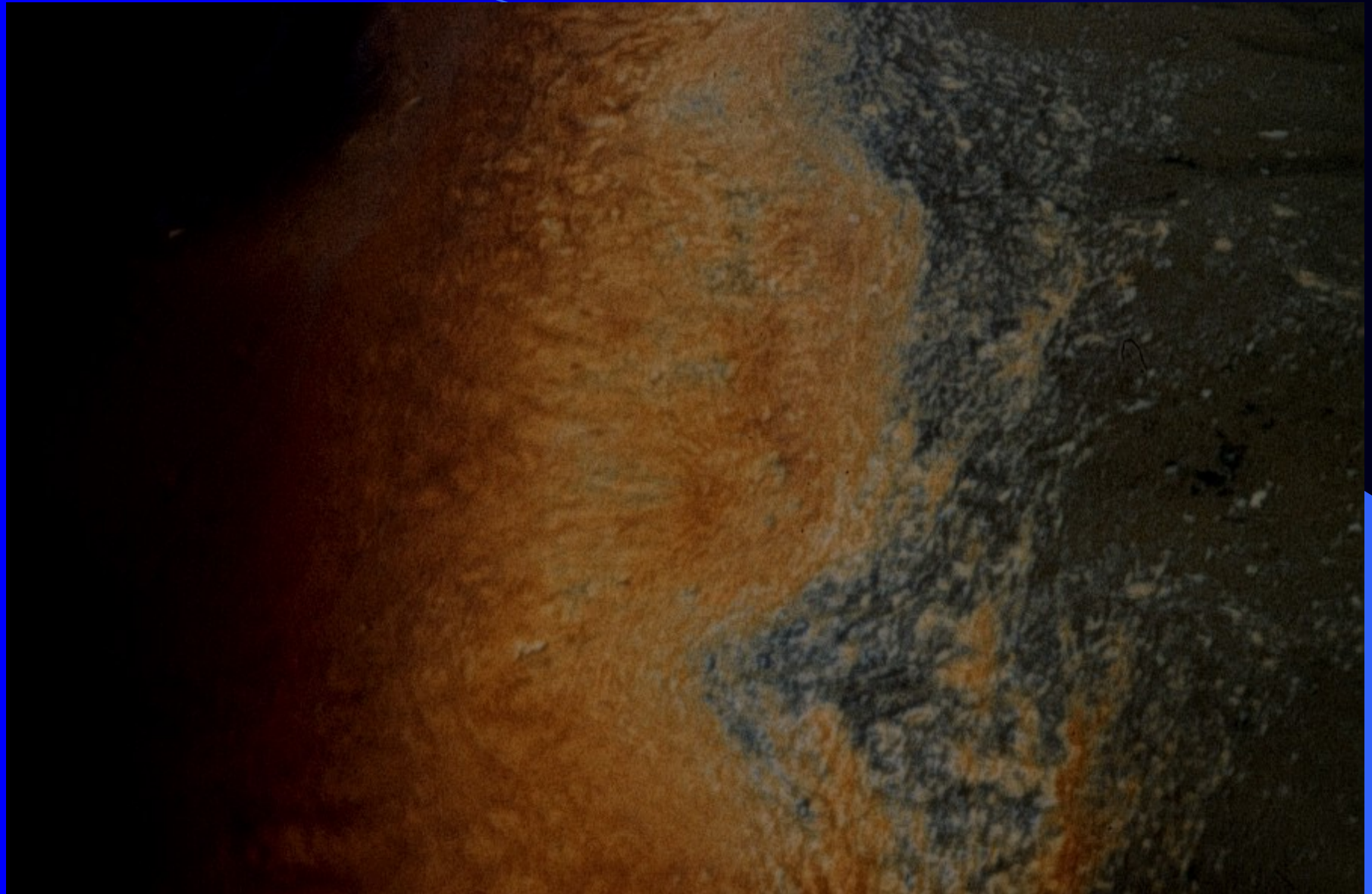
Water Content

- 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

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

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	$2 - 5.1 \times 10^6$
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 wife
- all water-in-oil states are emulsions
- water content can vary from 0 - 90
- all emulsions are the same
- water content is relevant or a discriminator

RIP - hopefully

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
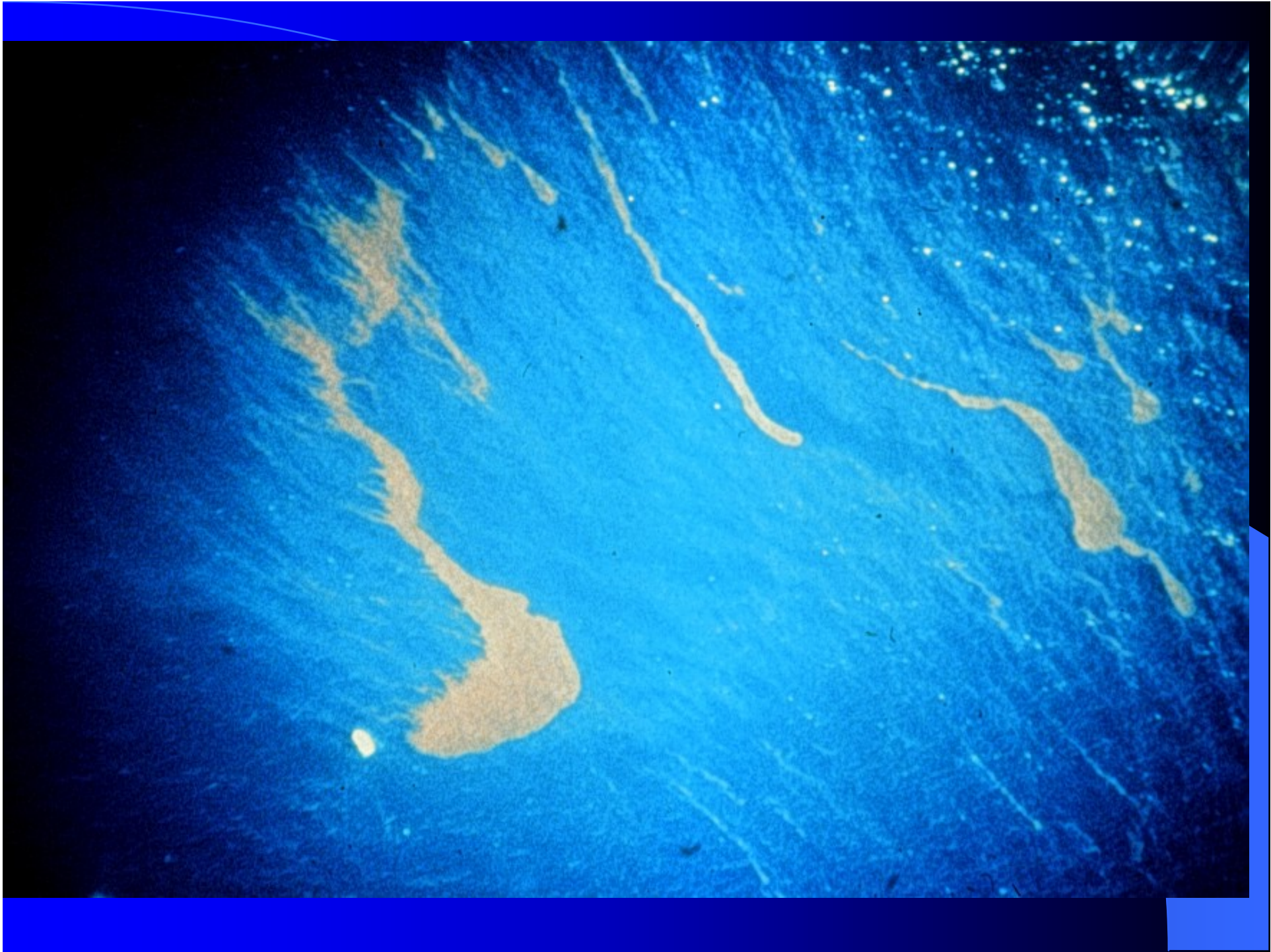
Natural Dispersion

- 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
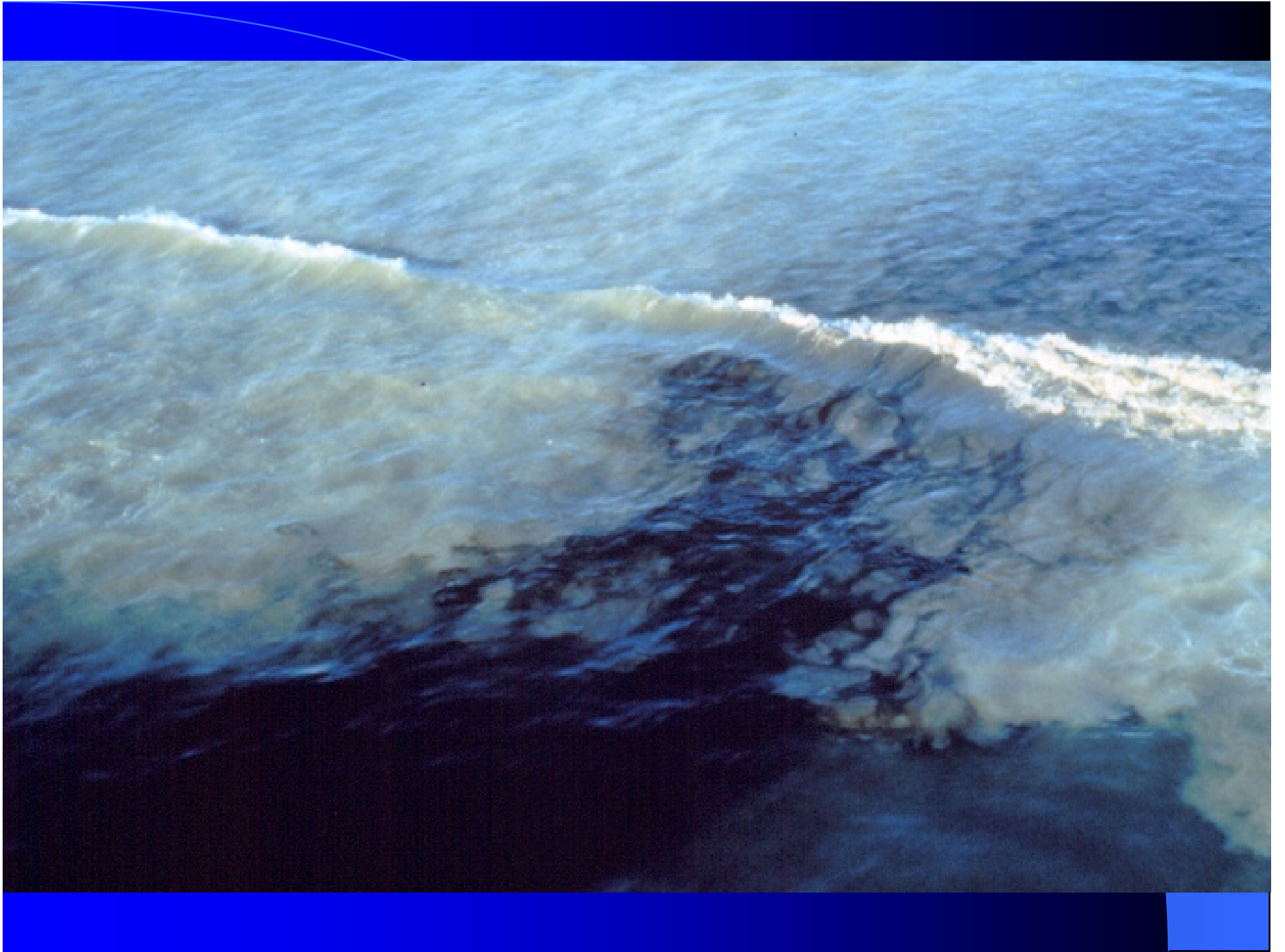
Dissolution

- 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