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Fate, Behavior & Modeling of Spilled Oil Sands Products
(Freshwater & Marine Environments)

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Introduction

Understanding Fate, Behaviour & Modelling

Behaviour Factors:

- Evaporation (and dissolution)
- Photo-oxidation
- Water Uptake and Emulsions
- Sediment Interactions and dispersion in water
- Temperature

Chemical changes to oil

- Evaporation
- Biodegradation

Open Questions

Oil Fate, Behaviour and Models

Model:

Quantitative or semi-quantitative prediction of oil movement in environment (trajectory), and transformation by environmental factors (weathering)

Oil Behaviour:

A physical/chemical transformation of the oil, a “weathering” process

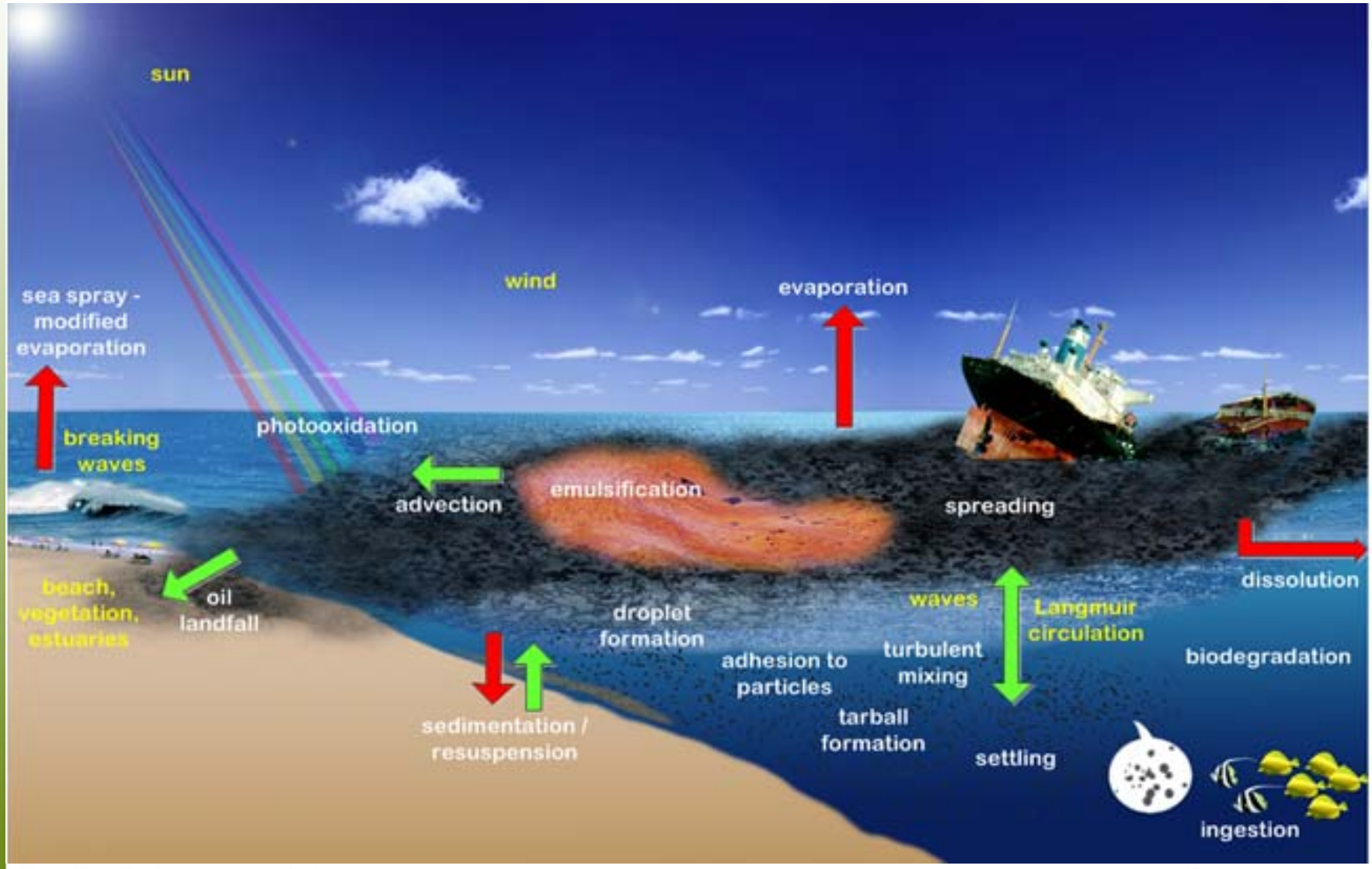
Oil Fate:

The eventual end-point state an oil may reach

Weathering

- In the environment crude oil and refined products are modified by natural physical, chemical, and biological processes that change their composition and fate.
- These processes are collectively referred to as weathering
- Primary processes include: evaporation, formation of emulsions, dissolution, photochemical and biological oxidation.
- The oil properties and how they change in the environment are one of the major drivers of oil behaviour (what it does), fate (where it goes), persistance (how long it lasts) and effects (who gets hurt).

Behaviour and Fate



Selected Physical Properties

Commercial Type		Heavy Sour Synbit	Sweet Synthetic Crude	Condensate	Heavy Sour Dilsynbit	Heavy Sour Dilbit	Light Sweet Crude
Oil		MacKay River Bitumen Diluted with Light Synthetic Crude Oil	Syncrude Synthetic Light Crude Oil	CRW Condensate	Albian Heavy Synthetic	Wabasca Heavy	West Texas Intermediate
Density (g/mL)	**0 ºC**				0.9463	1.0109	0.8594
	15 ºC	0.943	0.873	0.734	0.9372	0.9572	0.8474
Viscosity (mPa·s)	**0 ºC**				465	1007933	19.2
	15 ºC	241.9	6	0.6	156	128100	8.6
Flash Point	(ºC)	10	<-5	<-5	-23	151	-10
Pour Point	(ºC)	<-24	<-24	<-25	<-30	-6	-22
Sulfur	**(%)**				2.3	4.7	0.90%

Effects of Weathering on Models

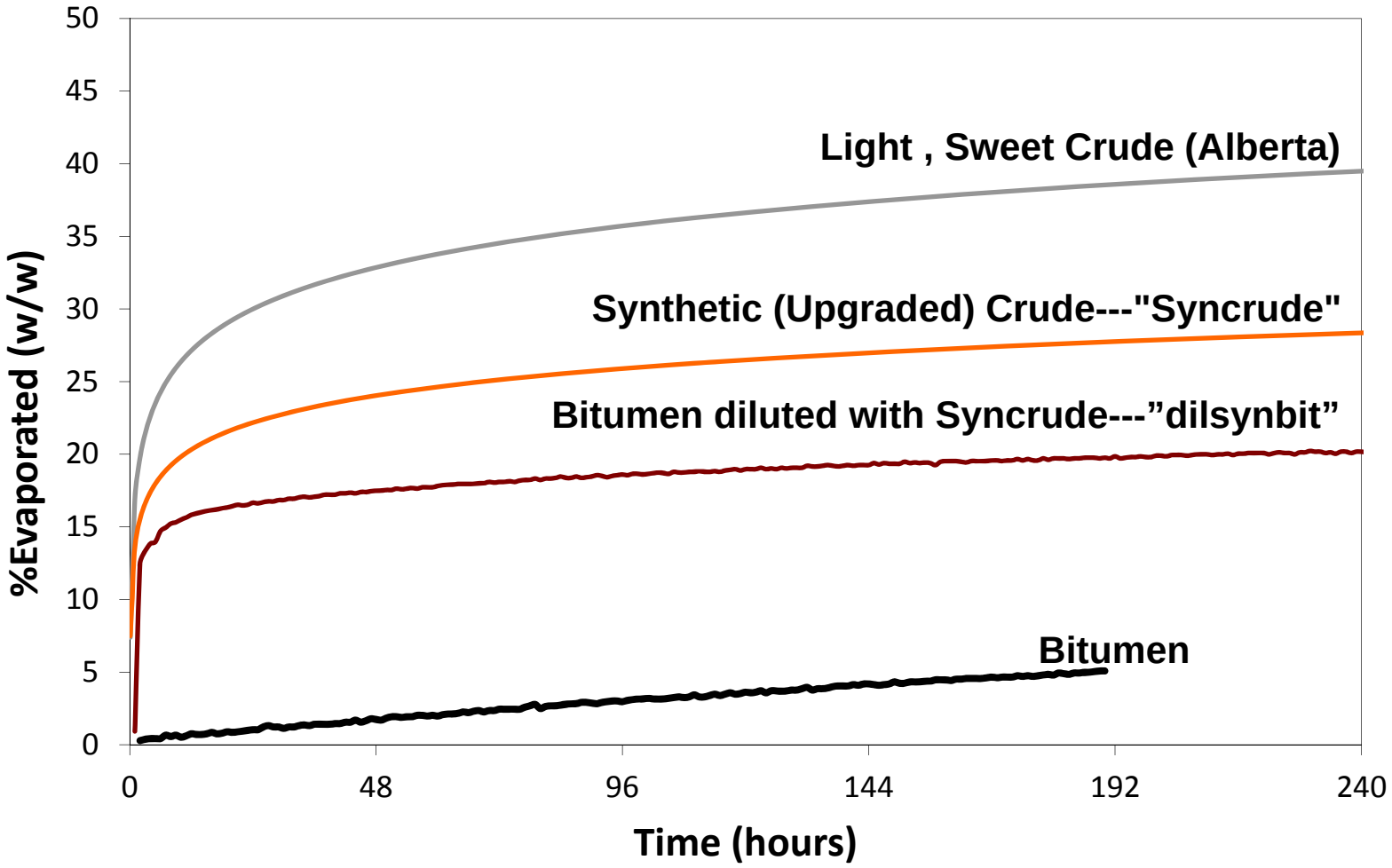
- Weathering affects oil characteristics, density, viscosity, surface/interfacial tensions
- Physical and chemical changes cause differences in trajectory behaviours and oil fate

Oil Type	Wind Drift or Leeway (%)
Gasoline	3--4
Diesel	3--4
Fresh IFO	3
Fresh Crude	3--4
Weathered IFO	2--3
Emulsified Oil	1--2
Scattered Tarballs	0.5--2

Factors: Evaporation

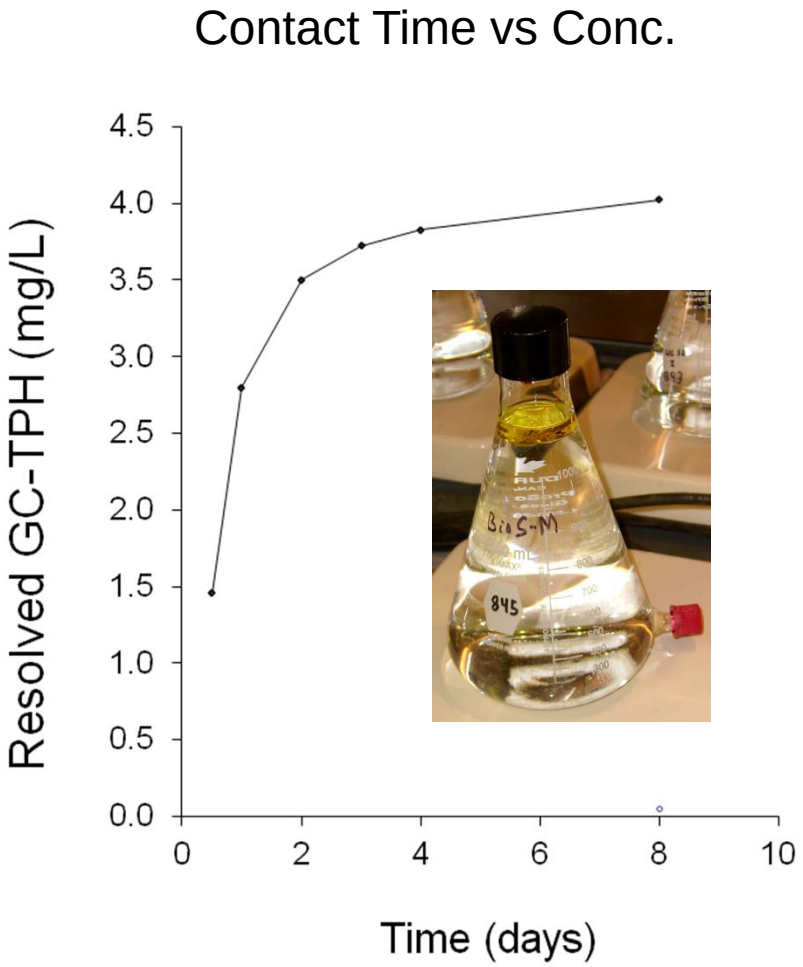
- Best understood weathering process.
- Evaporation is influential behavioural component
- A light crude can lose as much as 75% in two days and a medium crude as much as 40%
- A physical/thermodynamic process, molecules are removed from the oil, but not changed chemically.
- One of the best studied types of weathering, many major types of models for oil -> air evaporation.

Evaporation of Oil Sands Products



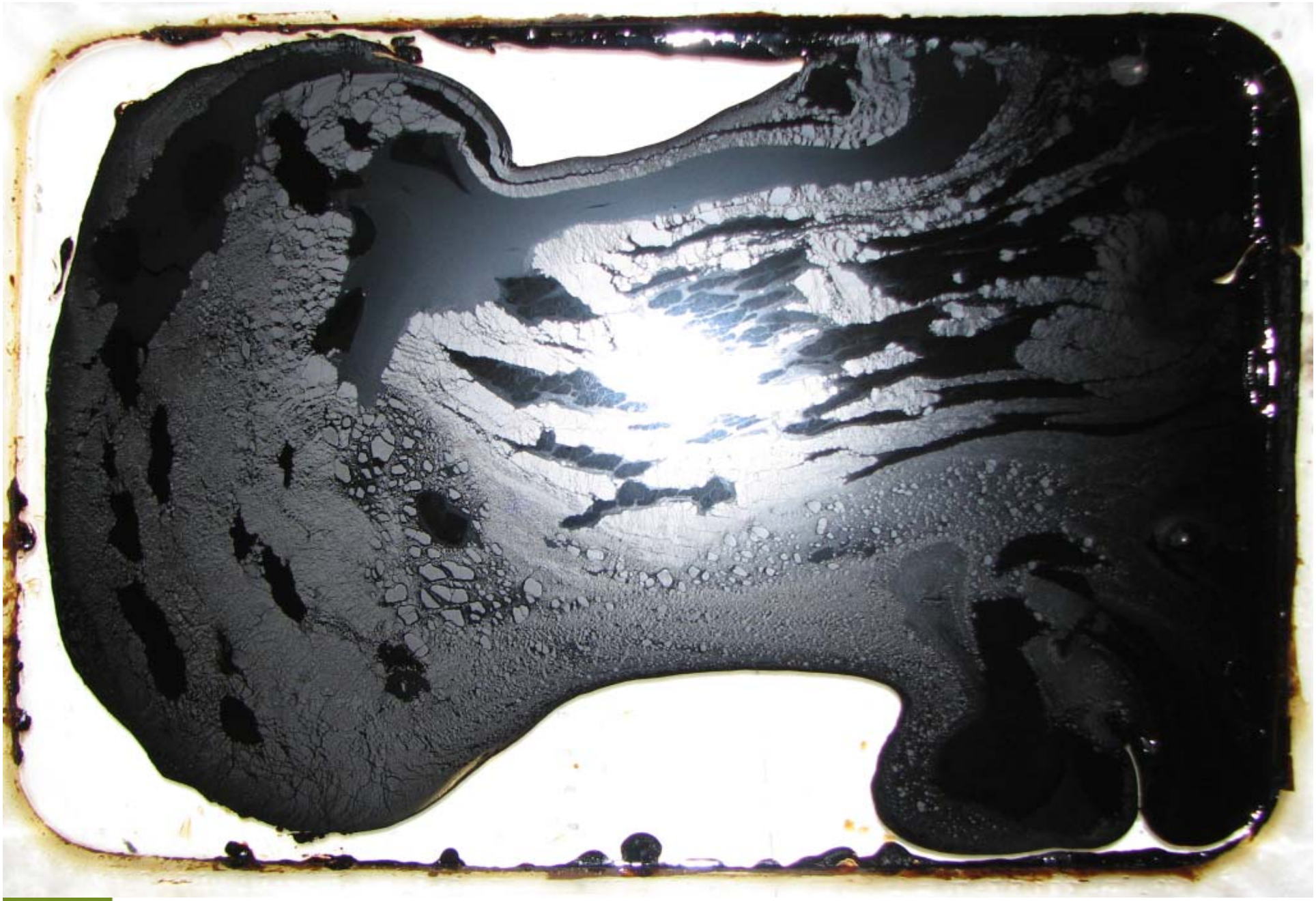
Dissolution and Solubility

- Not a major effect on oil behaviour, but can have large effects on organisms and habitats
- Affected by oil concentration, mixing energy, temperature and time
- Can be limited by diffusion rates through oil
- Physical models well developed



Factors: Photo-oxidation

- Observed to cause increase in density in real-world spills
- "Skin" formation
- Appears to increase oxidized components of oil
  - Enhances water uptake and emulsion formation
- No models for behaviour



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Factors: Water Uptake

- Formation of finely dispersed water droplets in an oil phase --- Emulsions and other dispersions
- Oil densities increase, viscosities greatly increase
- Changes state of oil, but not chemistry.
- Changes transport: oil is lower in water, has higher stickiness and much higher viscosity
- “Entrained water”– simple viscosity-bound water in oil – may persist for significant amounts of time
- Models for water uptake and retention are not well developed --- all data is empirical/experimental

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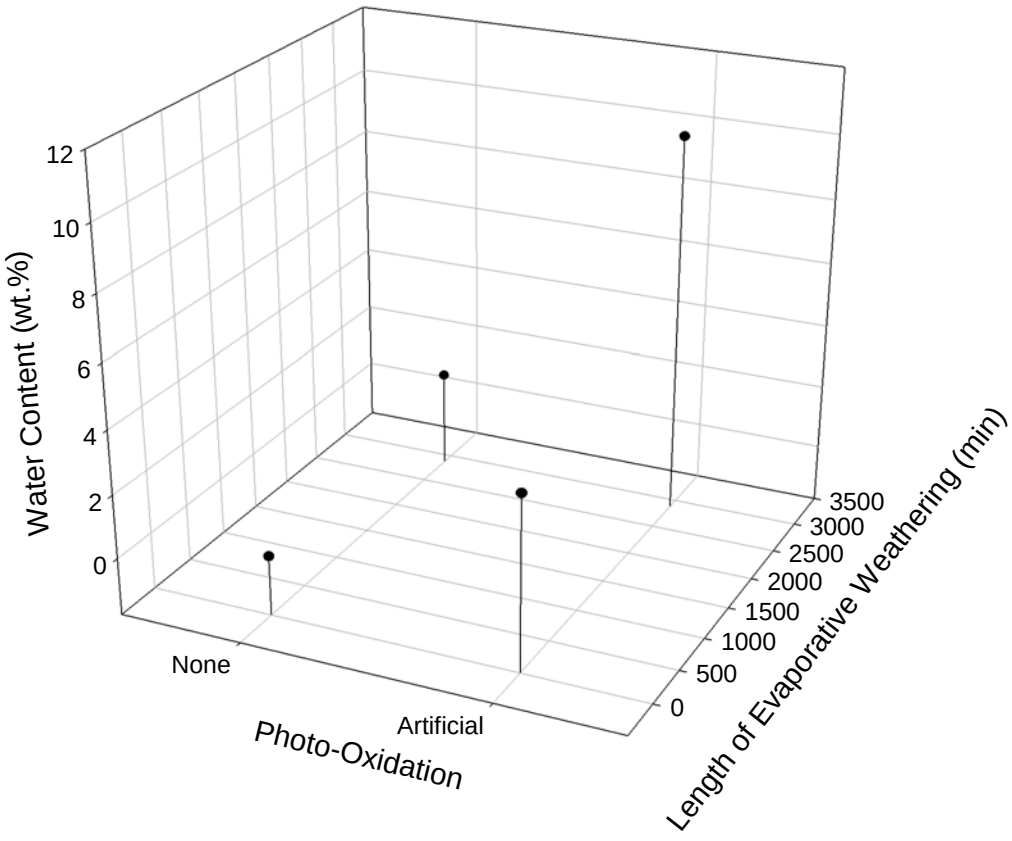
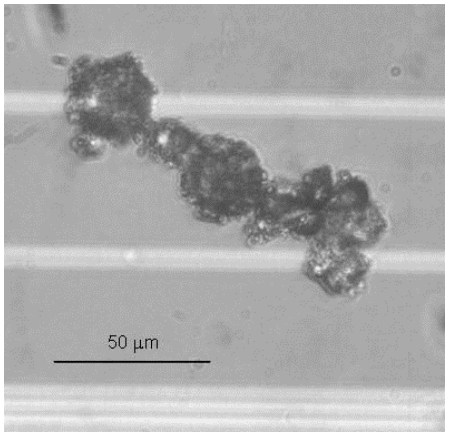
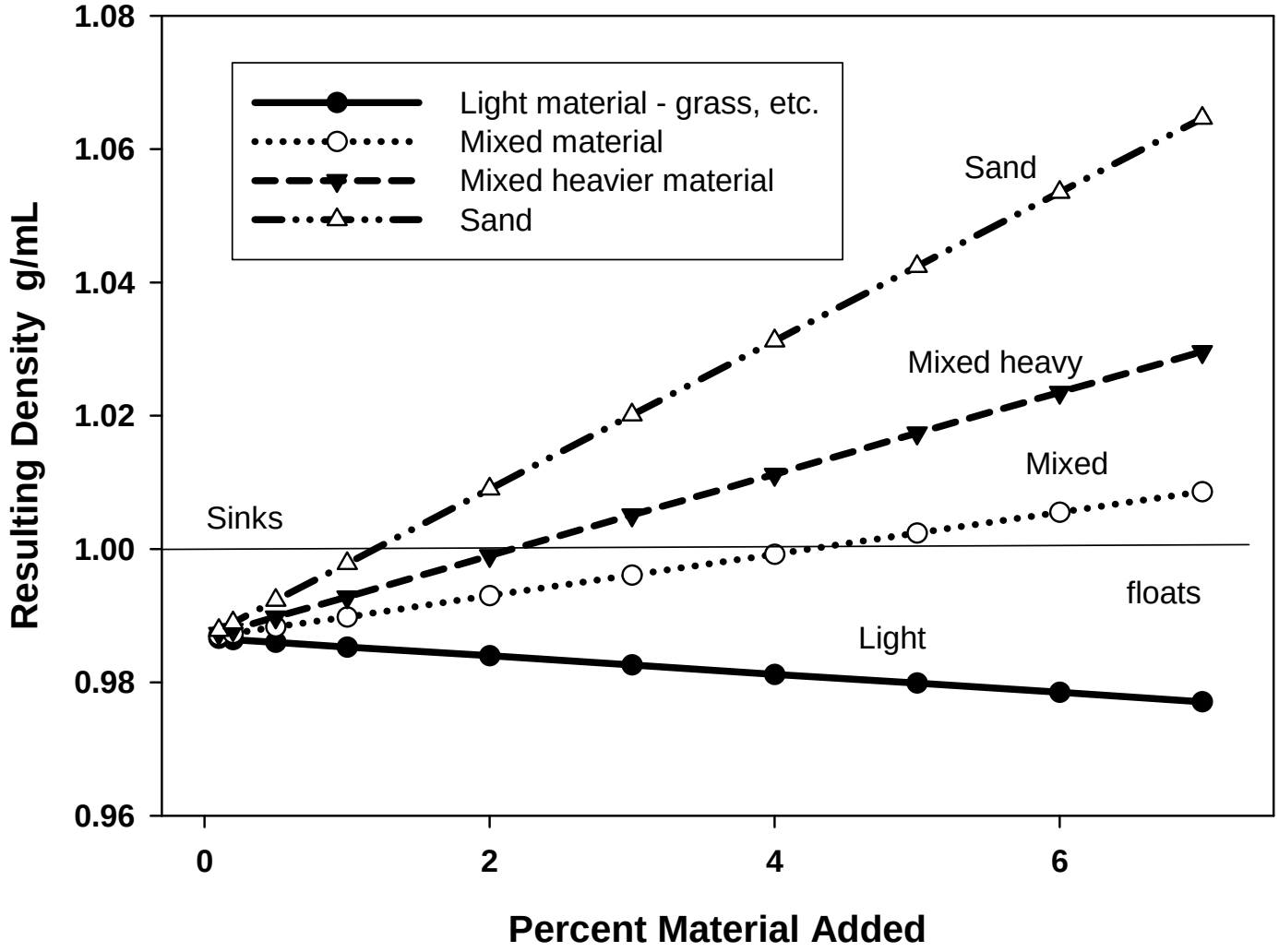
Evaporation and Photo-oxidation Effects on Water Content of Oil



Factors: Sediment Interaction

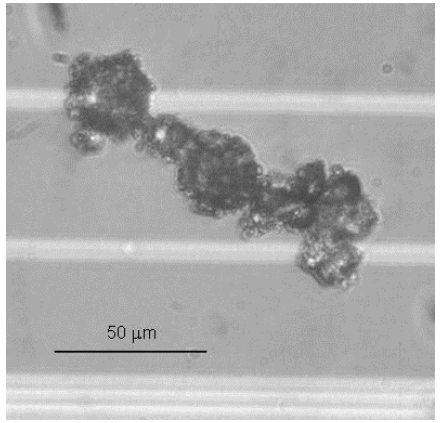
- Observed sedimentation of sunken oil at several spills
  - Quantitative data from spills of opportunity is sparse.
- Quantitative models just now starting to be developed
- Several modes of uptake
  - Suspended particulates (OMA/OFI/OSA/SPM, etc...)
  - Surf-zone interactions




Light material - grass, etc.
Mixed material
Mixed heavier material
Sand
Sand
Mixed heavy
Mixed
Sinks
floats
Light
Resulting Density g/mL
1.08
1.06
1.04
1.02
1.00
0.98
0.96
0
2
4
6
Percent Material Added

Dispersion and Sediment Interaction

- Dispersion of oil into small droplets occurs in high-energy environments: breaking waves, storms, floods, surf zones.
- Dispersion can promote rapid weathering because of proportionately large surface areas to volume of oil
  - Dissolution
  - Emulsification
  - Sediment uptake
  - Water uptake
- Sinking and “tarball formation”
- Models are under active development



Khelifa et al, 2008

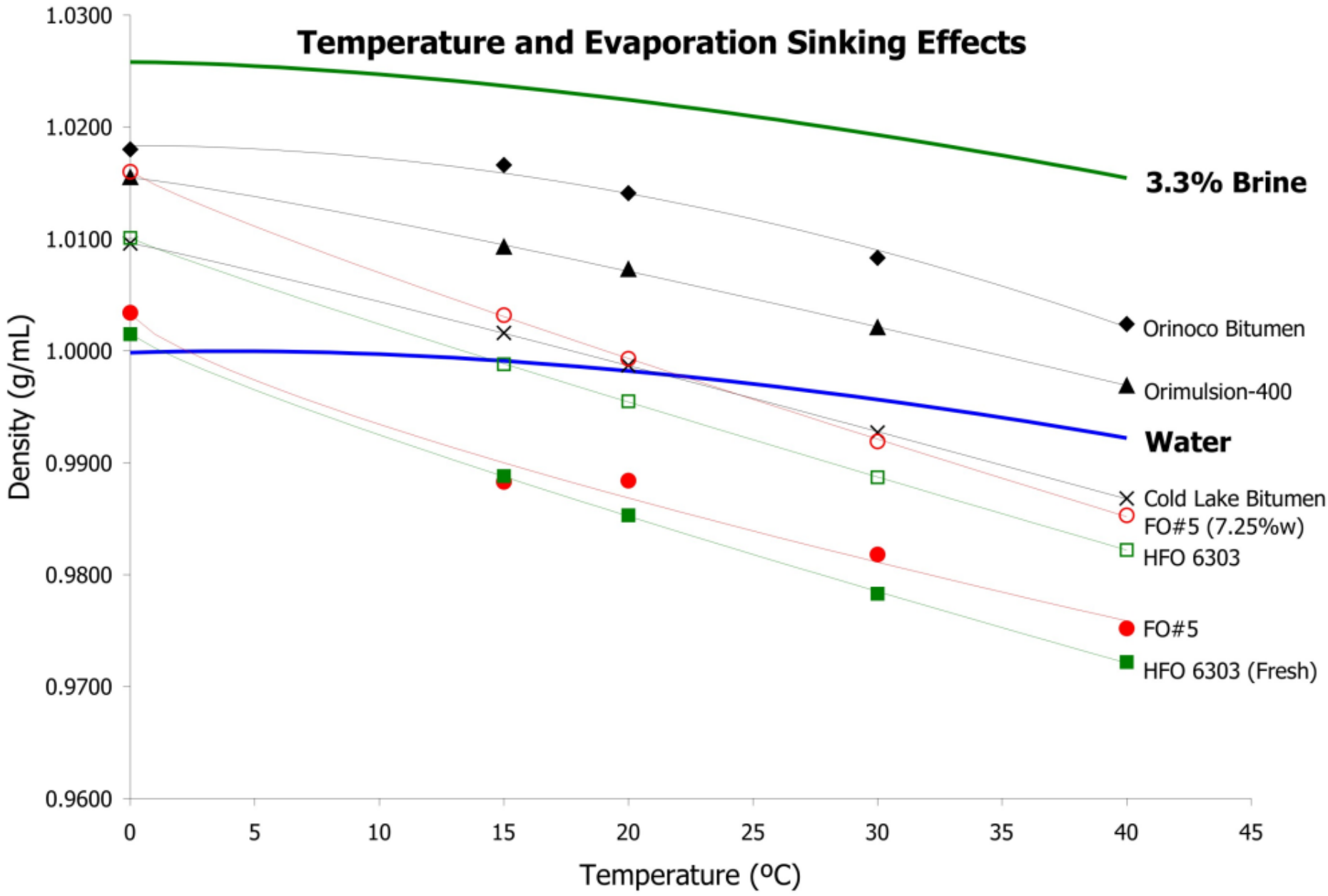
Water Surface

Immediately After Agitation

A Few Minutes Later

Factors: Temperature

- Oil density increases with decreasing temperature
- Cyclic - daily and seasonal variations, with additional weather factors
- Temperature affects many oil properties (viscosity, interfacial tensions)
  - Potential for non-linear interactions
- Empirically well understood, practical models exist



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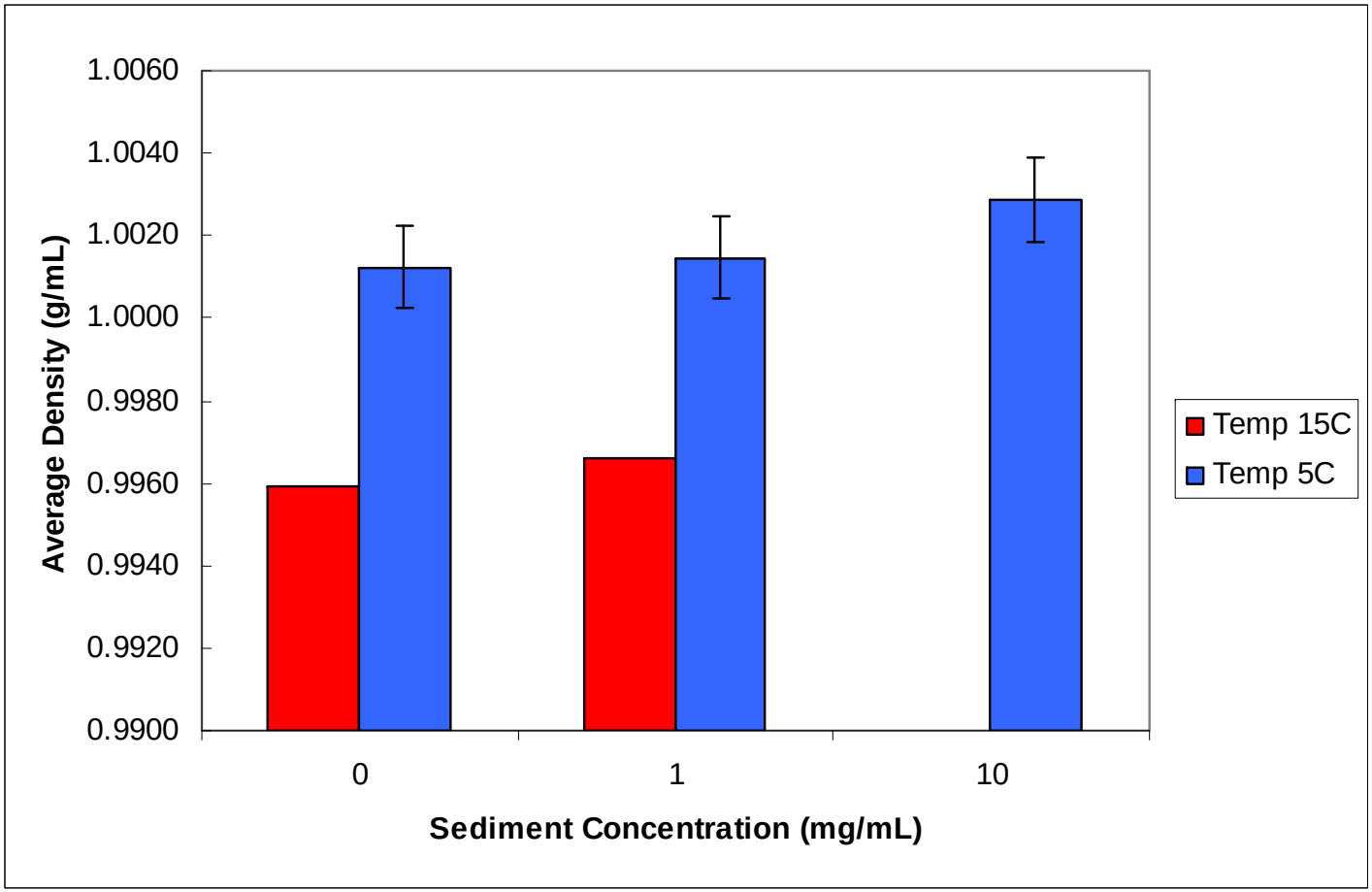
Sediment Uptake vs Temperature



Chemical Weathering

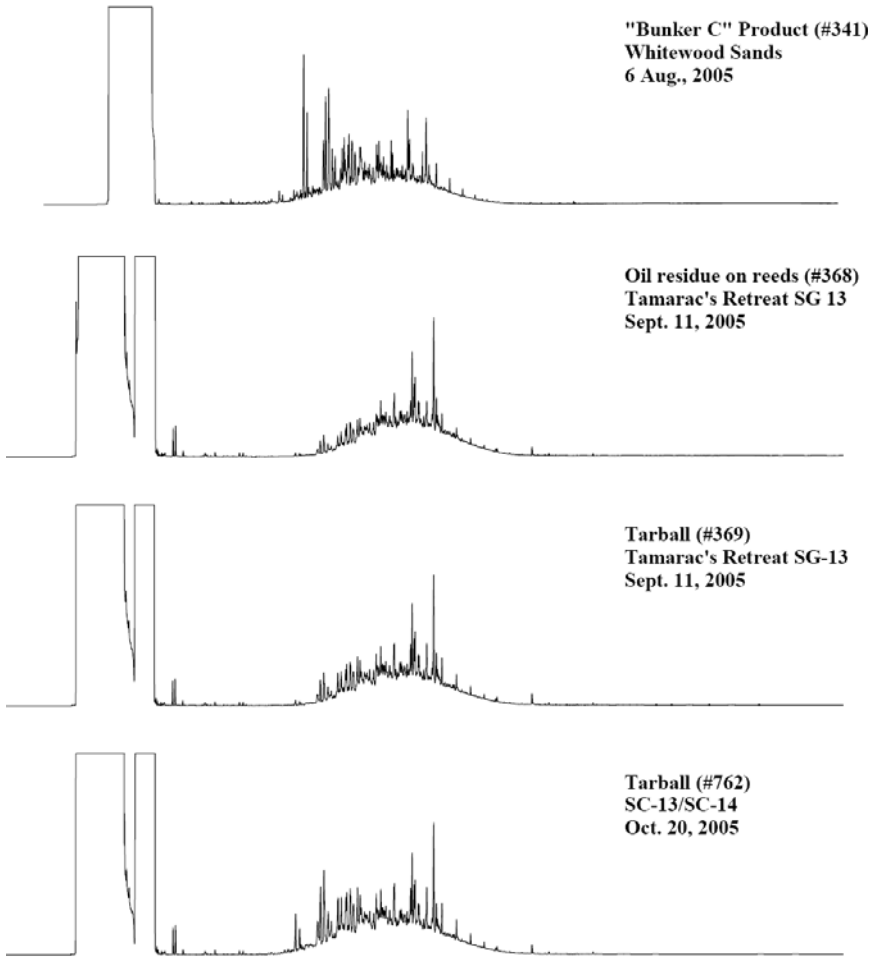
- Chemical distribution of oil changes in the environment.

  Removal:
  - Evaporation
  - Dissolution and dispersal

  Transformational:
  - Chemical degradation/oxidation (eg photo-enhanced)
  - Biological degradation

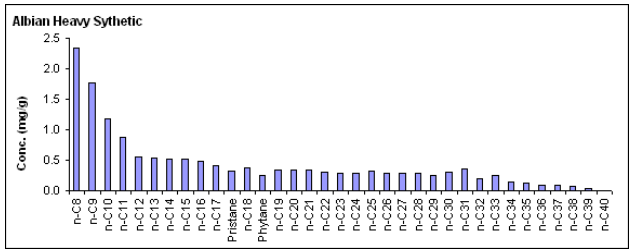
Weathering changes to oil

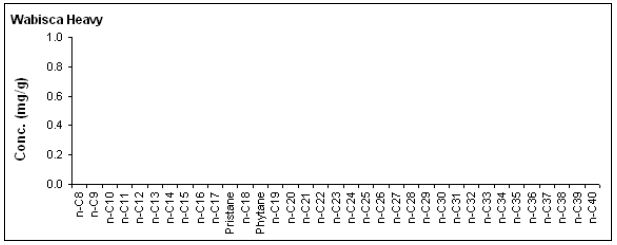
- Largest changes occur rapidly after spill, with slow degradation later
- Rapid removal of light ends <C25 (F1 + F2)
- The fate of the oil strongly affects degradation
- Densities uniformly increased with exposure
- Oil does not weather evenly; highly degraded skins can contain less weathered oil.
- Models are mostly empirical

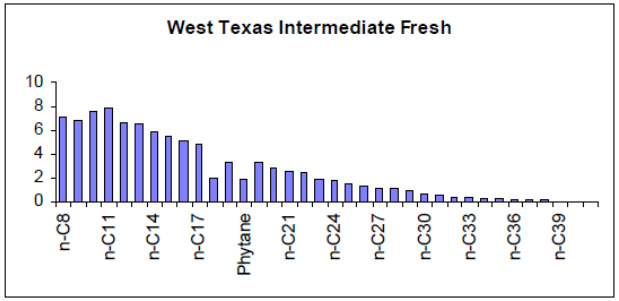


Chemistries---Fresh oils

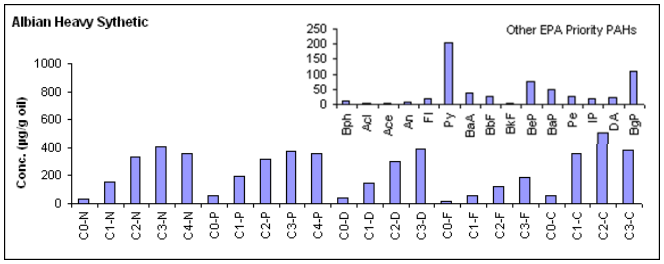
Saturate n-Alkanes

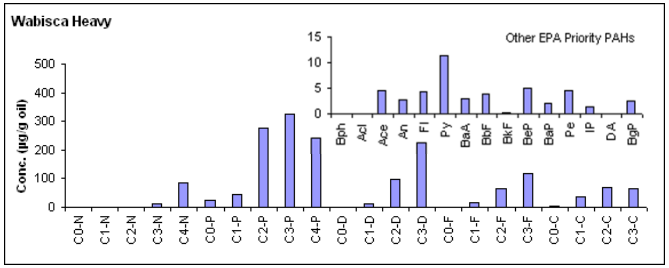


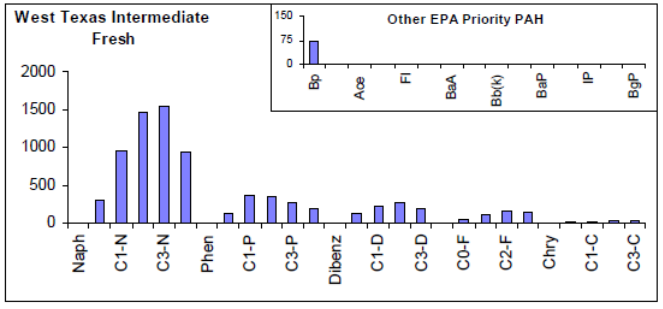




Polycyclic Aromatic Hydrocarbons (PAH)

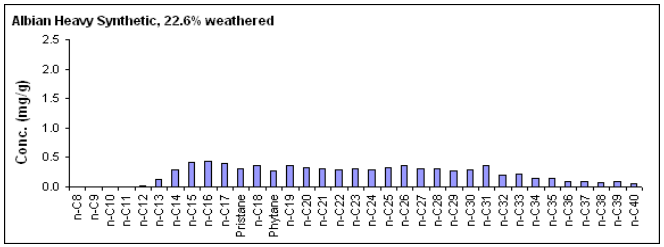


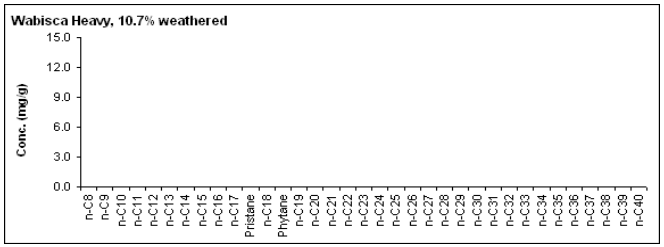


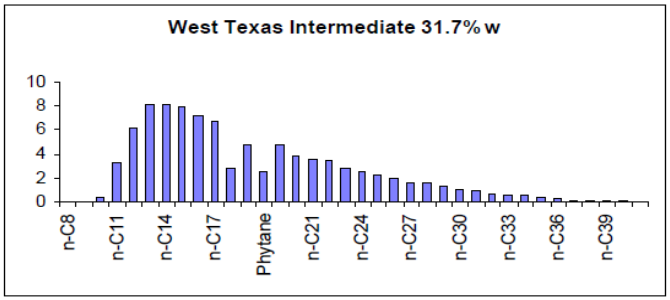


Effects of Evaporation

Saturate n-Alkanes







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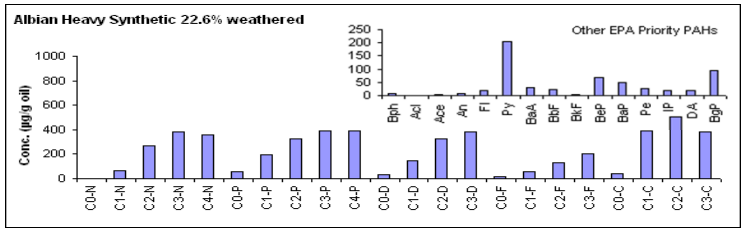
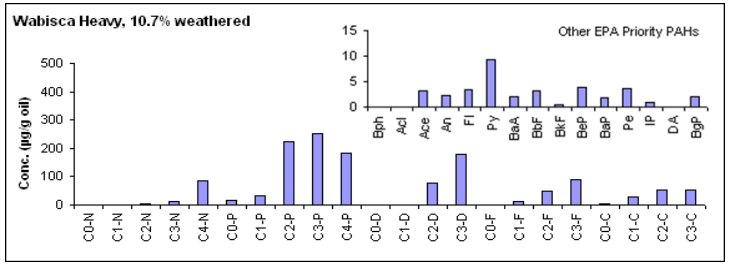
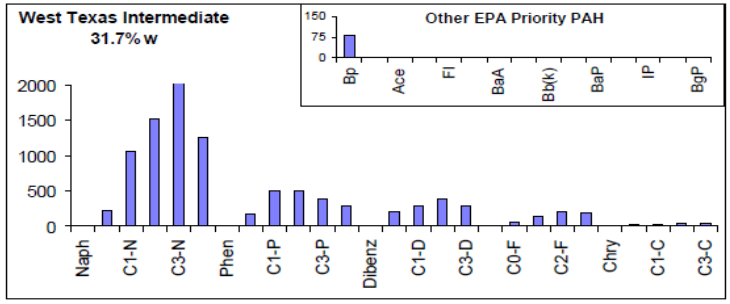


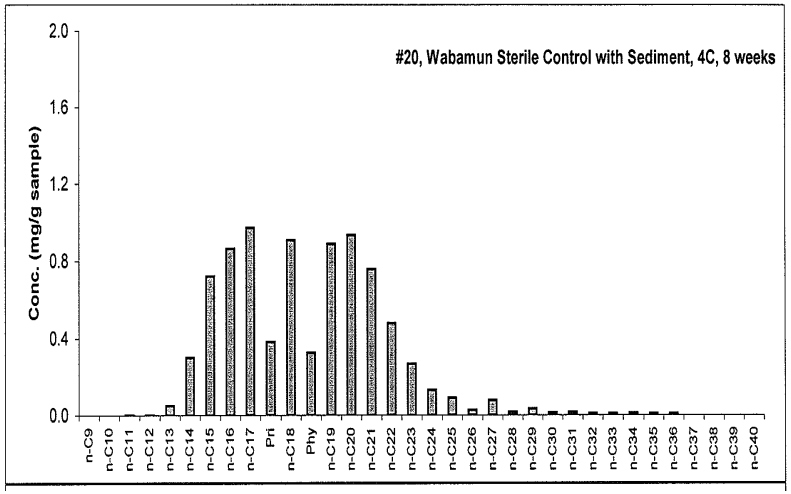


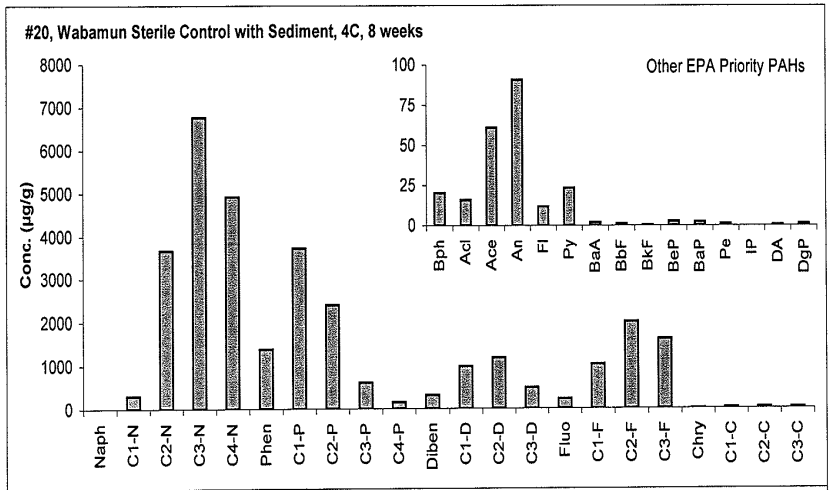


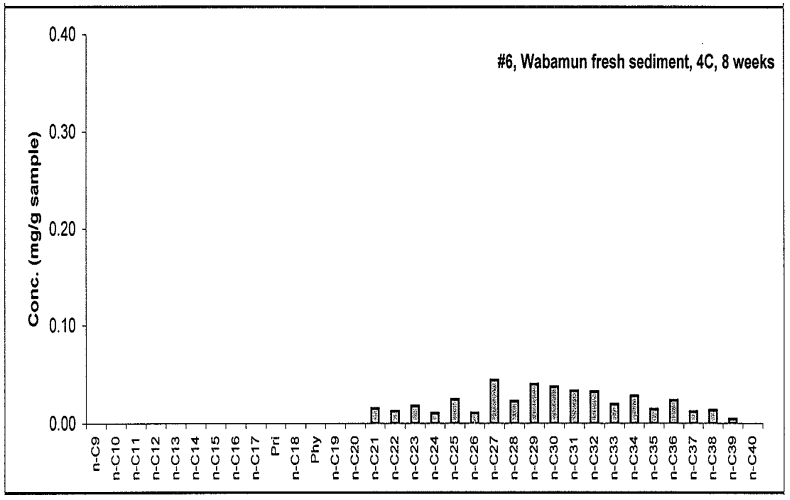
Biodegredation

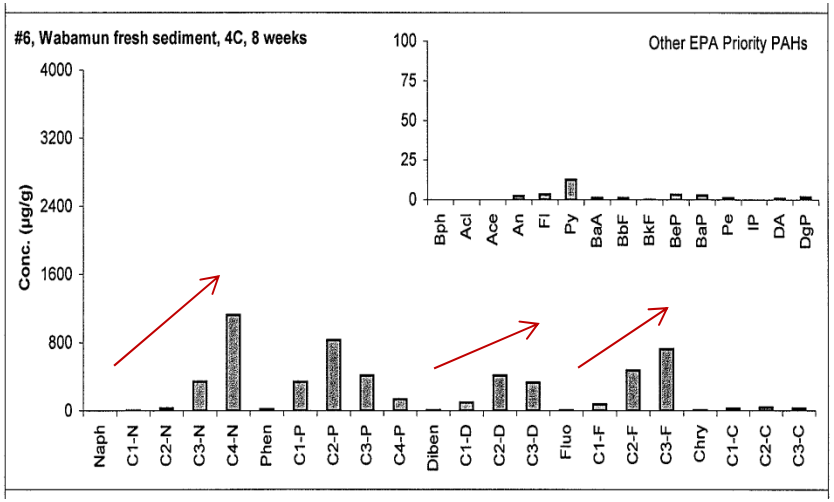
- Long-term action of microbes on oil
- Almost reverse of photo-oxidation: smaller molecules affected first, straight-chain alkanes preferred, followed by unalkylated aromatics.
- Can last for months to years.
- Aerobic can be much faster than anaerobic.
- Availability of fertilizers and electron acceptors

Biodegradation of Heavy Oil

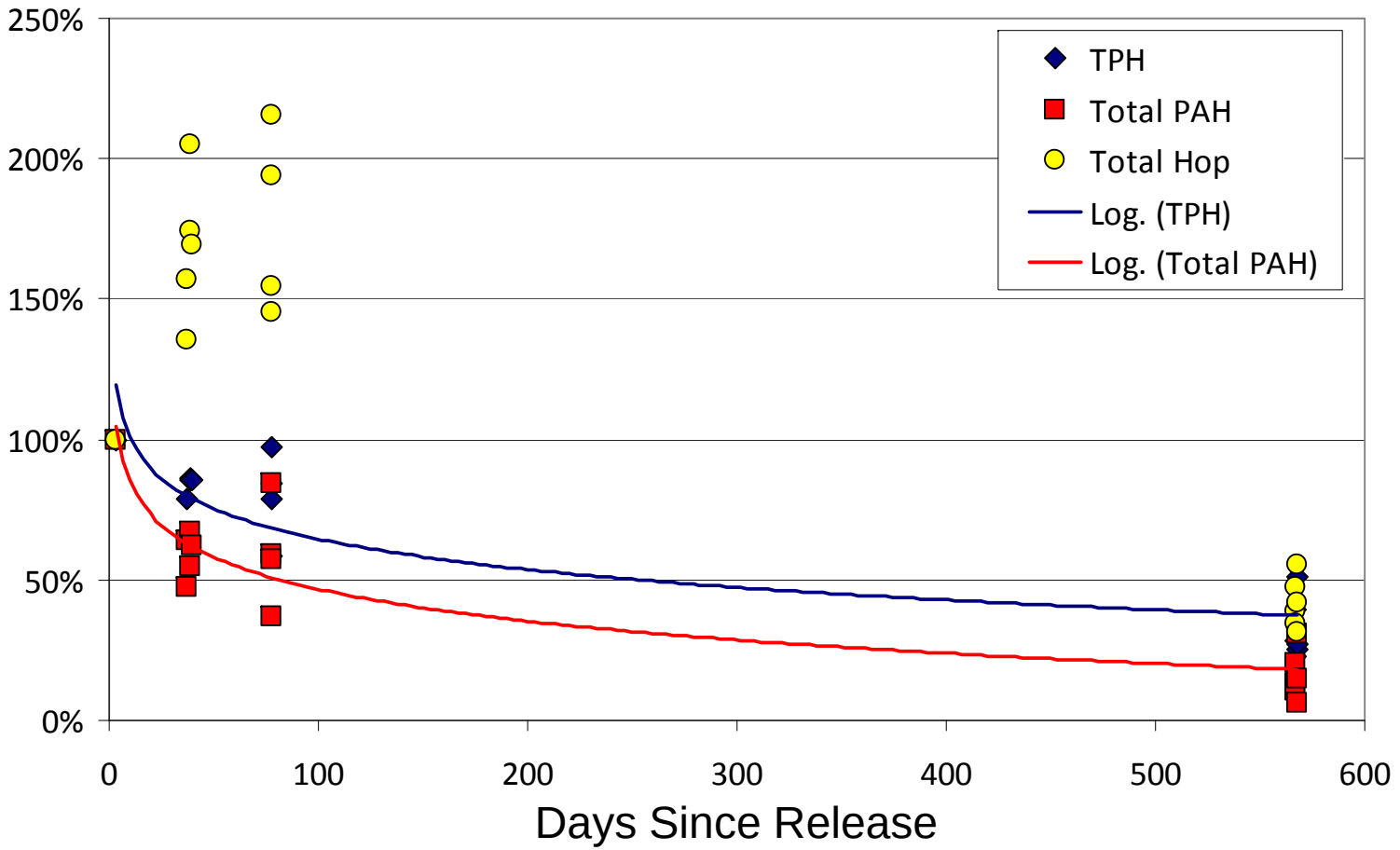








Bio-oxidation in natural samples



Hollebone et al, 2011

Open Questions

- Changes to dilbit chemistry by evaporation of diluent components (rate of change)
- Dispersion of oil in water (droplet size, rise time, coalescence)
- Resuspension and remobilization potential
- Dissolution in water & bioavailability
- Toxicity, chemical and physical
- Persistence
- Interactions of factors to affect behaviours

Questions? Comments?

END