SPILLED OIL FATE and BEHAVIOR

Objectives

- Understand what an oil is
- Learn the basic properties of oil and how they effect the behavior and fate of oil
- Understand the types of oil
- Understand oil weathering mechanisms
- Understand how oil properties effect response actions

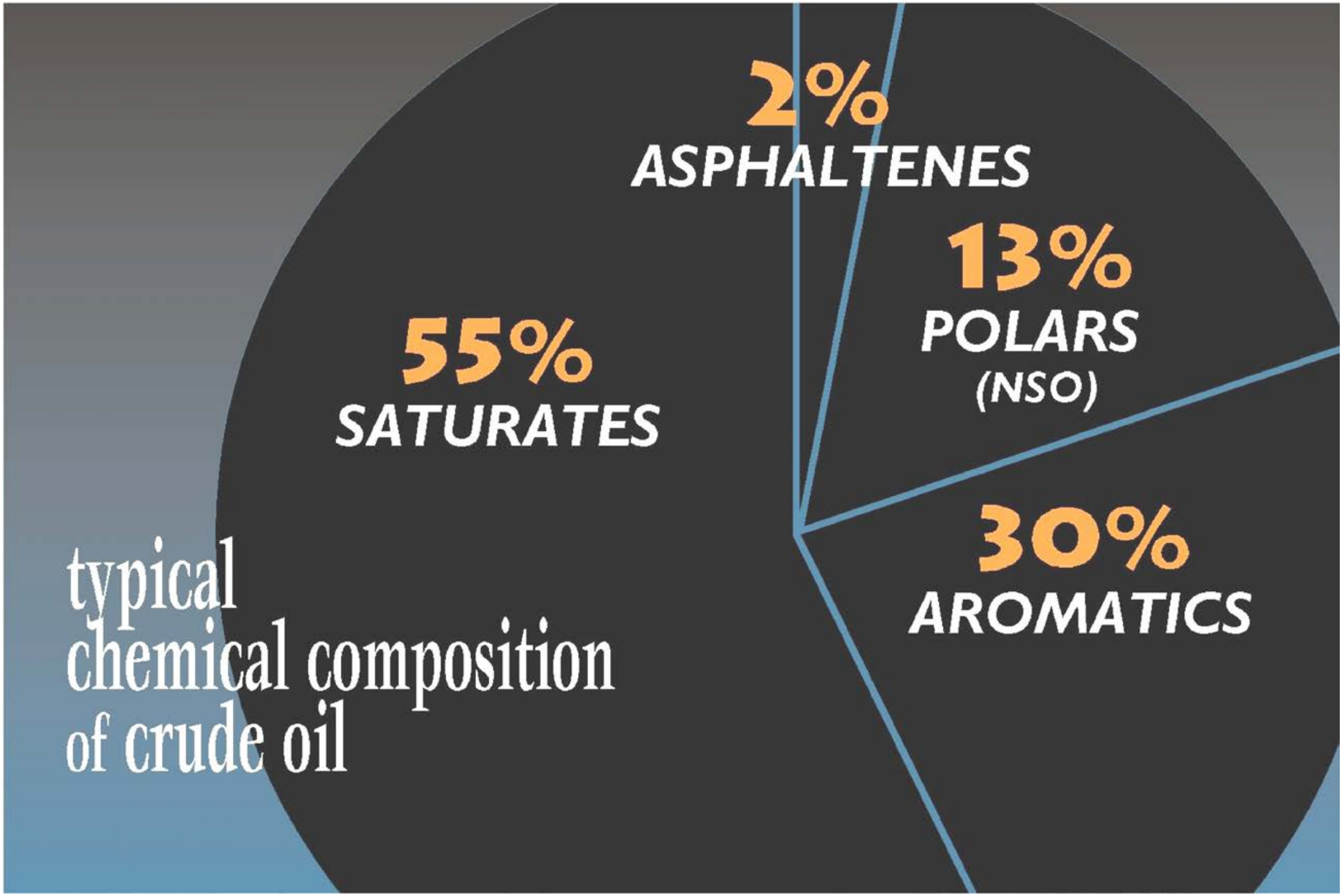
3 Major Types of Oil

- Petroleum Oils
  - Crude/Refined /Blended
- Non-petroleum Oils
  - Animal/Vegetable/Bio-diesel
- "Odd-ball" Oils
  - Transformer/Silicone/Synthetic

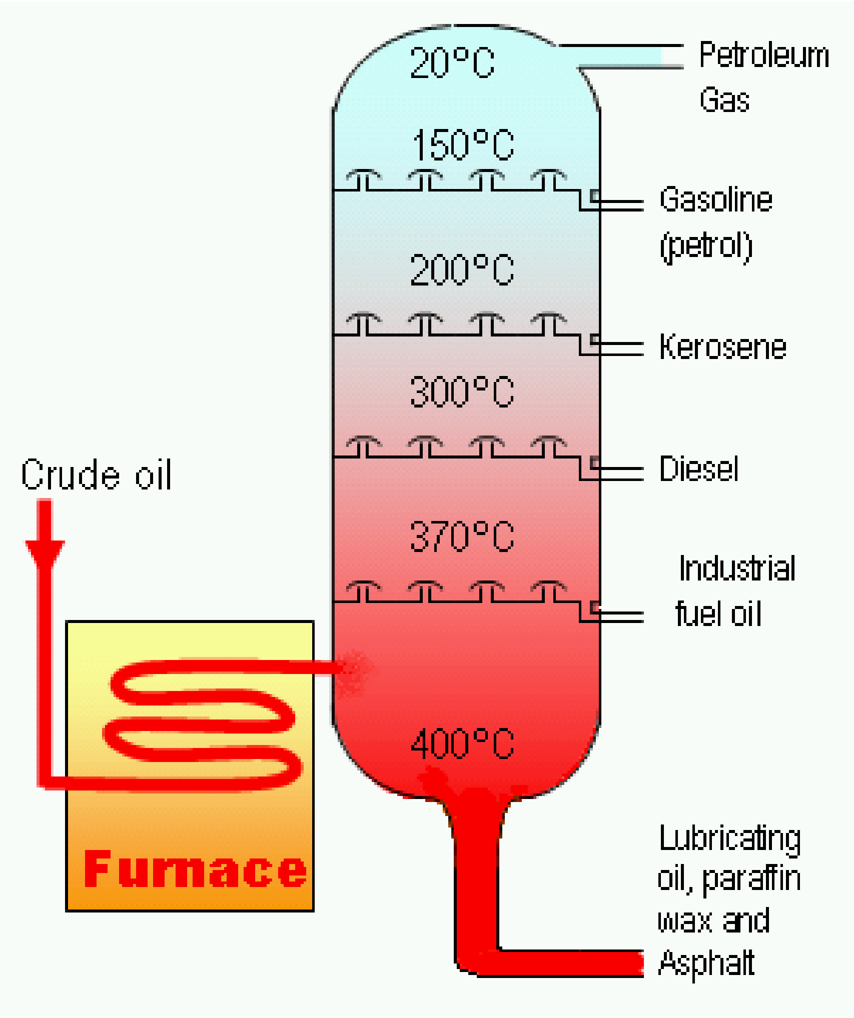
Petroleum is…

- …naturally occurring?
- …Solid, liquid, or gas?
- …a chemical?
- …the basic building block for millions of different chemicals and compounds

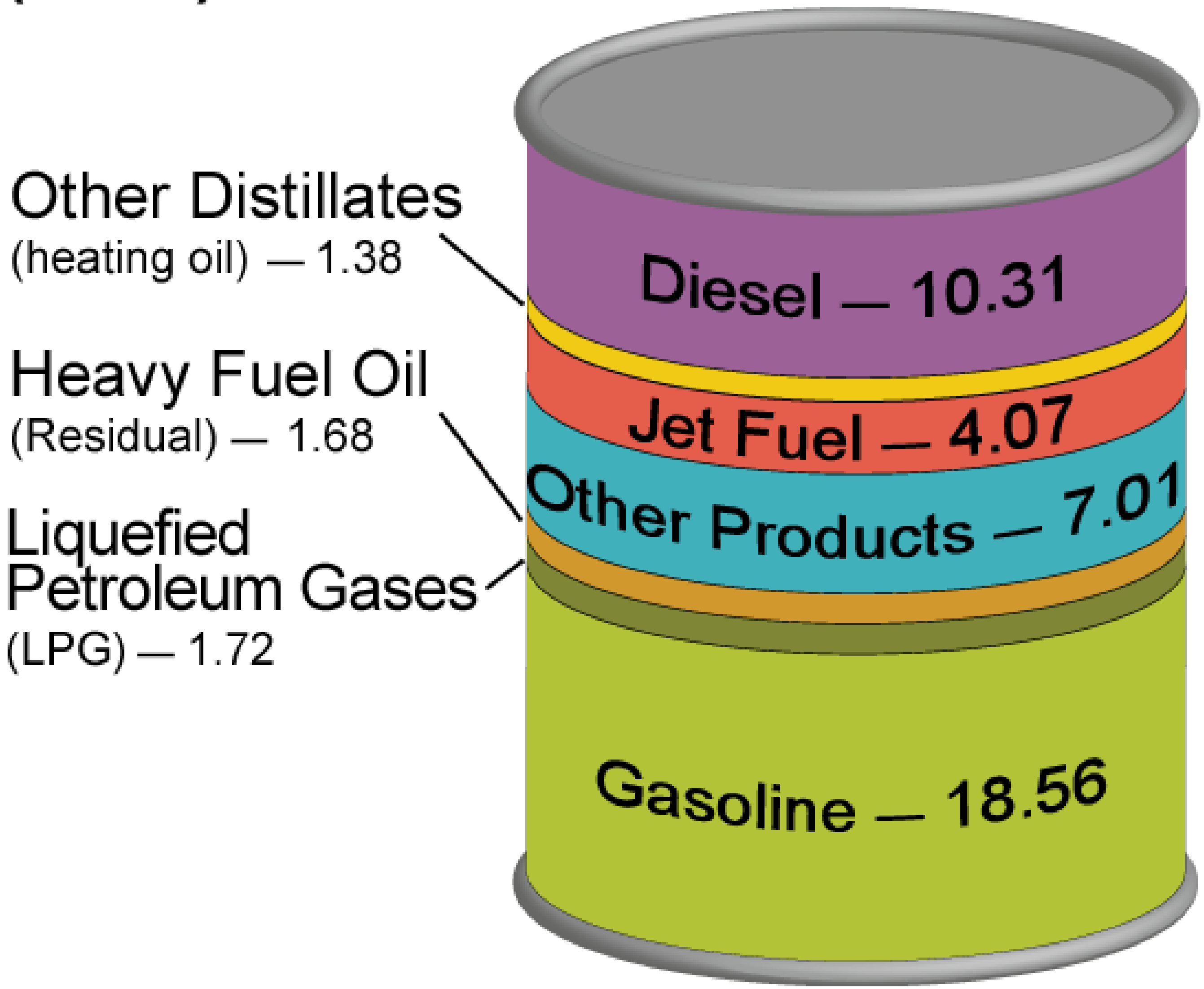
What is Crude Oil?



Refining Crude oil into Products



Products Made from a Barrel of Crude Oil (Gallons) (2008)



Physical and Chemical Properties which affect cleanup and behavior on water

- Density
- Surface tension
- Viscosity
- Pour point
- Flash point
- Solubility in water
- And how these parameters change with time
- These parameters are measured at “standard temperature and atmospheric pressure – SPILLS AREN’T

Oil Groups

Group 1	Gasoline Products
Group 2	Diesel-like Products/Light Crude Oils
Group 3	Medium Crude Oils/Intermediate Products
Group 4	Heavy Crude Oils/Residual Products
Group 5	Non-floating Oils

Classification by Group (°API)

Group I	°API > 45
Group II	°API 35 – 45
Group III	°API 17.5 – 35
Group IV	°API 10 – 17.5
Group V	°API < 10 (LAPIO)

Specific Gravity (s.g.)
s.g. = wt. of oil/wt. of “pure” water

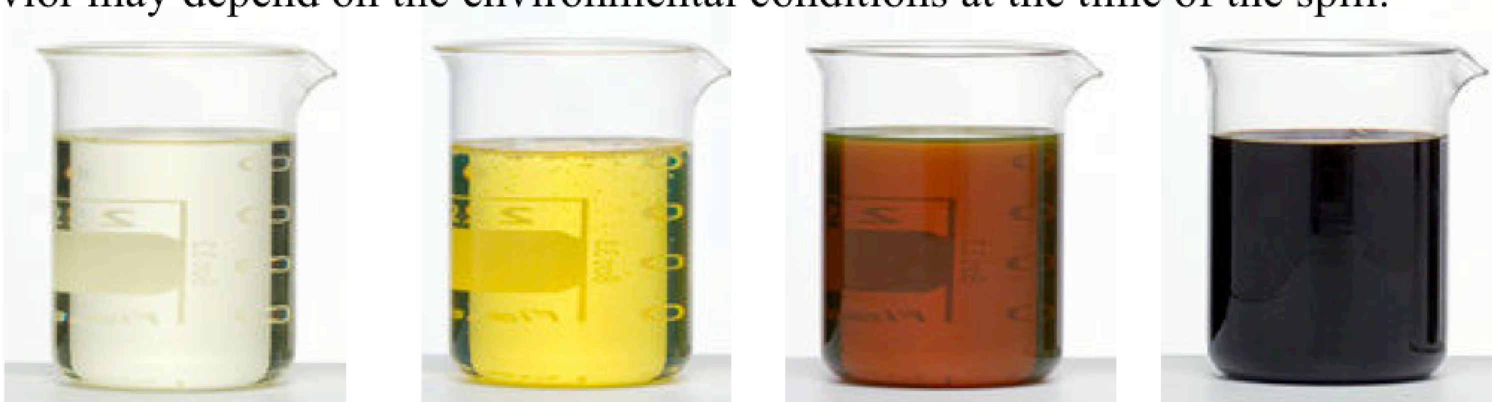
Formula: °API = (141.5/s.g.) – 131.5
10°API = 1.000 s.g. or pure water at 60°F

Low API Gravity Oil (LAPIO)

	Density	Viscosity (general)	Pour Point	Flash Point	Solubility into fresh water
Group 1 (gasoline)	0.75	Thinner than water	–120°F to – 240°F	– 45°F	Up to 200 ppm
Group 2 (diesel)	0.80 – 0.85	Milk	–13°F	126°F	Up to 200 ppm
Group 3 (med crude)	0.85 – 0.95	Anti-Freeze		20°F – 90°F	2 – 40 ppm
Group 4 (heavy crude)	0.95 – 1.0	Molasses	~50°F – 100°F	>400°F	2 – 40 ppm
Group 5 (non-floating)	≥ 1.0	Peanut butter??		NA	2 – 40 ppm

How toxic are different oil types?

Different oil types have different physical properties, chemical composition and toxicity, and their behavior may depend on the environmental conditions at the time of the spill.

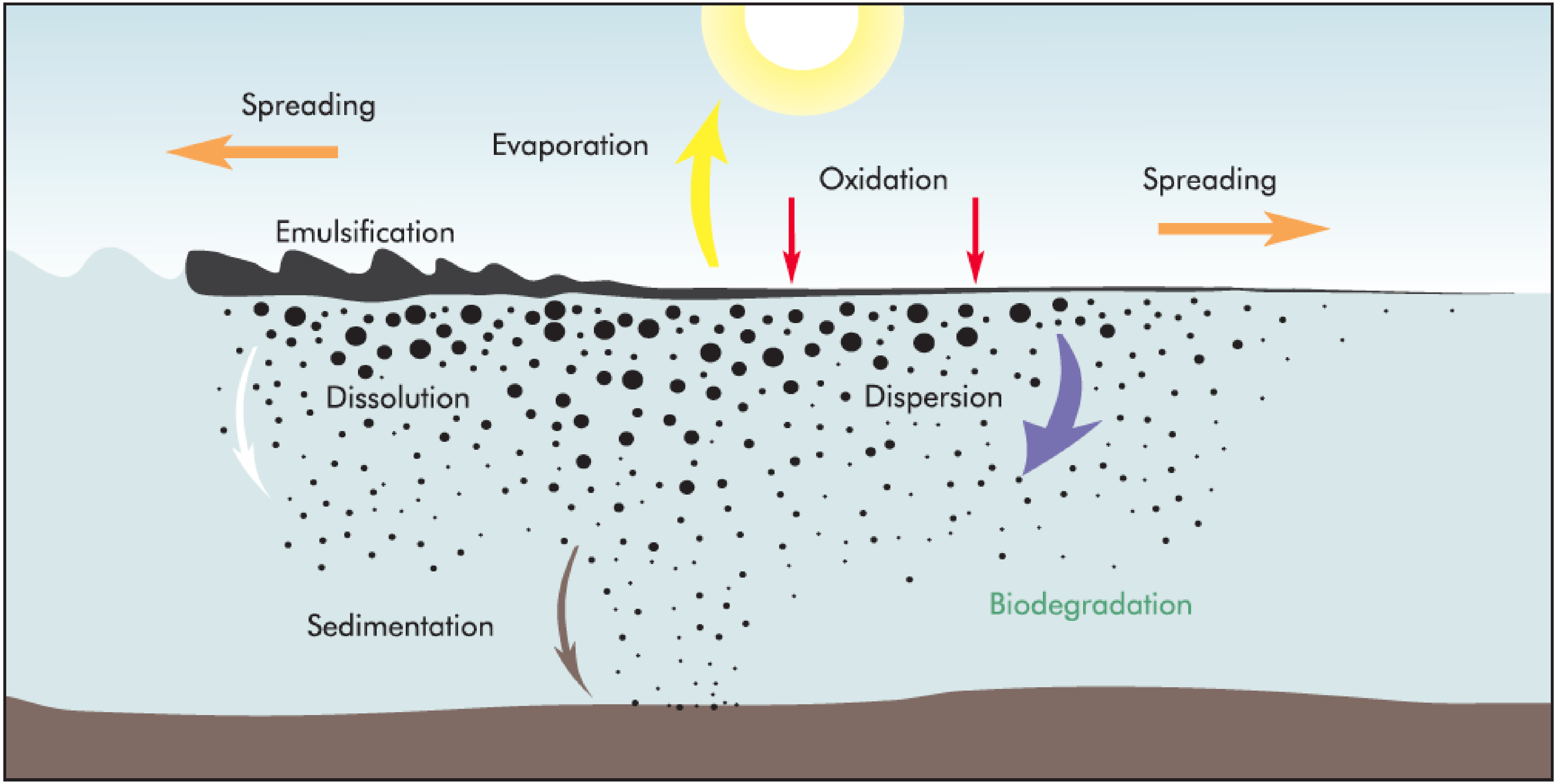


Oil type	**Class I:** Very Light	**Class II** Light	**Class III** Medium	**Class IV** Heavy
Examples	Gasoline	Diesel and light crudes	Paraffin-based oils, most crude oils	No. 6. fuel oils, heavy crudes
Acute toxicity to aquatic organisms	High toxicity from soluble compounds	Moderate toxicity from soluble compounds	Moderate to low toxicity	Low toxicity, but high risk of smothering
Long term environ. effects	Likely not severe	May cause long-term intertidal contamination	May cause severe long-term impacts Can severely impact bird, fur-bearing mammals, and shoreline habitats	Possible long-term sediment contamination Can severely impact bird, fur-bearing mammals, and shoreline habitats

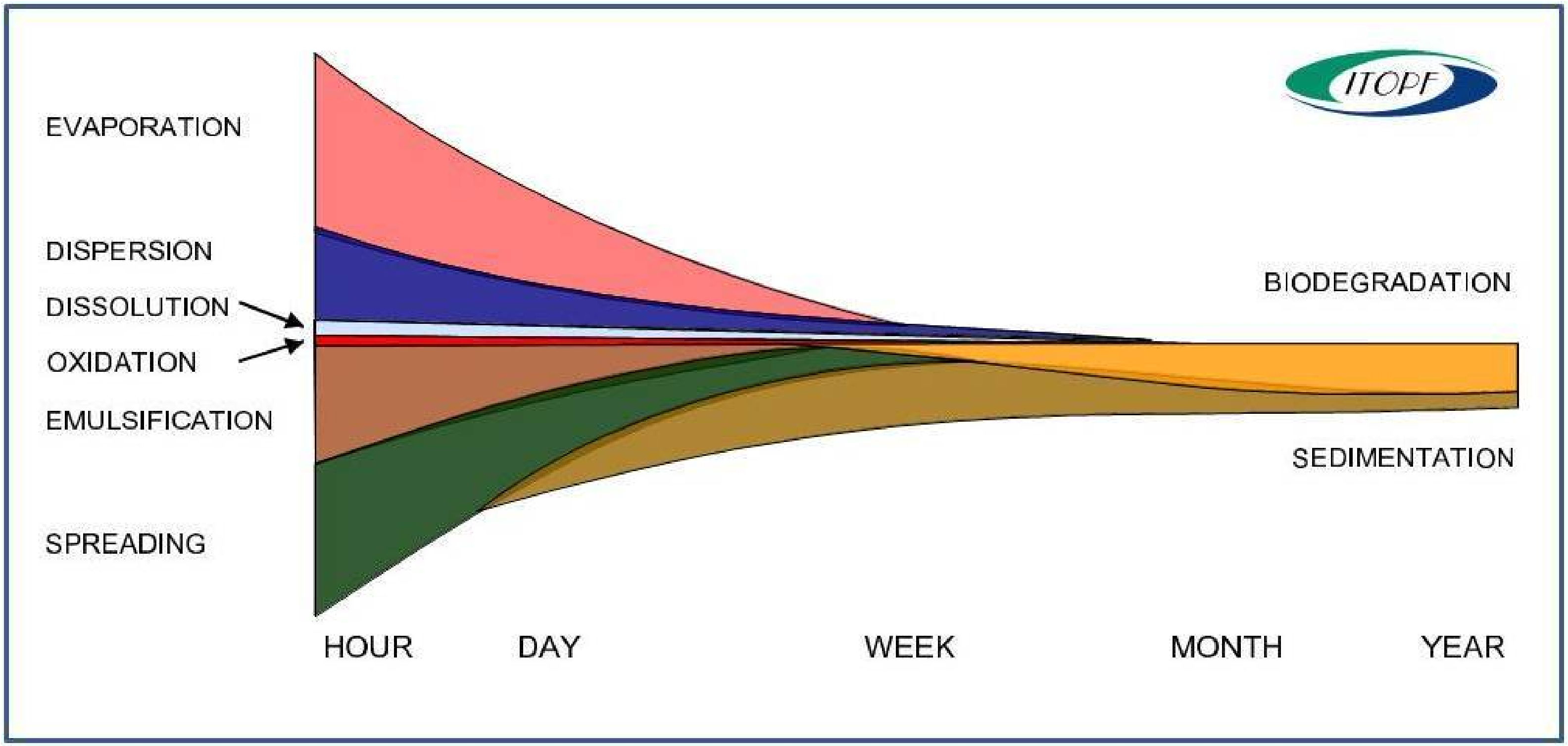
Weathering

- Spilled oil's exposure to the environment results in a series of *changes in physical and chemical* properties…known as **weathering**
- Weathering *starts immediately* upon oil being spilled, and weathering is ***usually highest in the first few hours of the spill***
- Weathering occurs as the oil spreads and moves

Weathering (dynamics)



Characteristics of Oil After a release

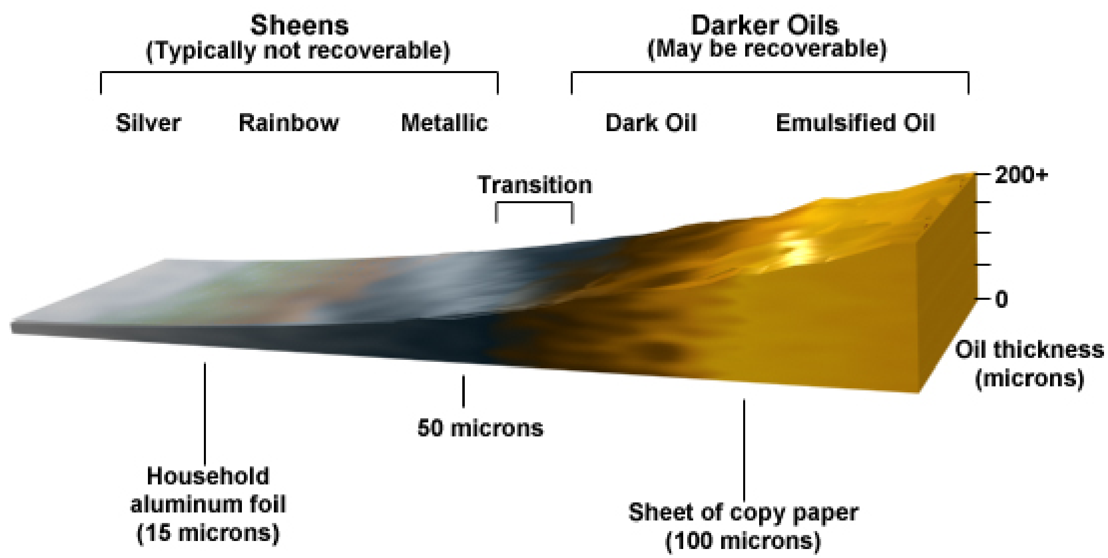


Source: International Tanker Owners Pollution Federation Ltd

Weathering Processes

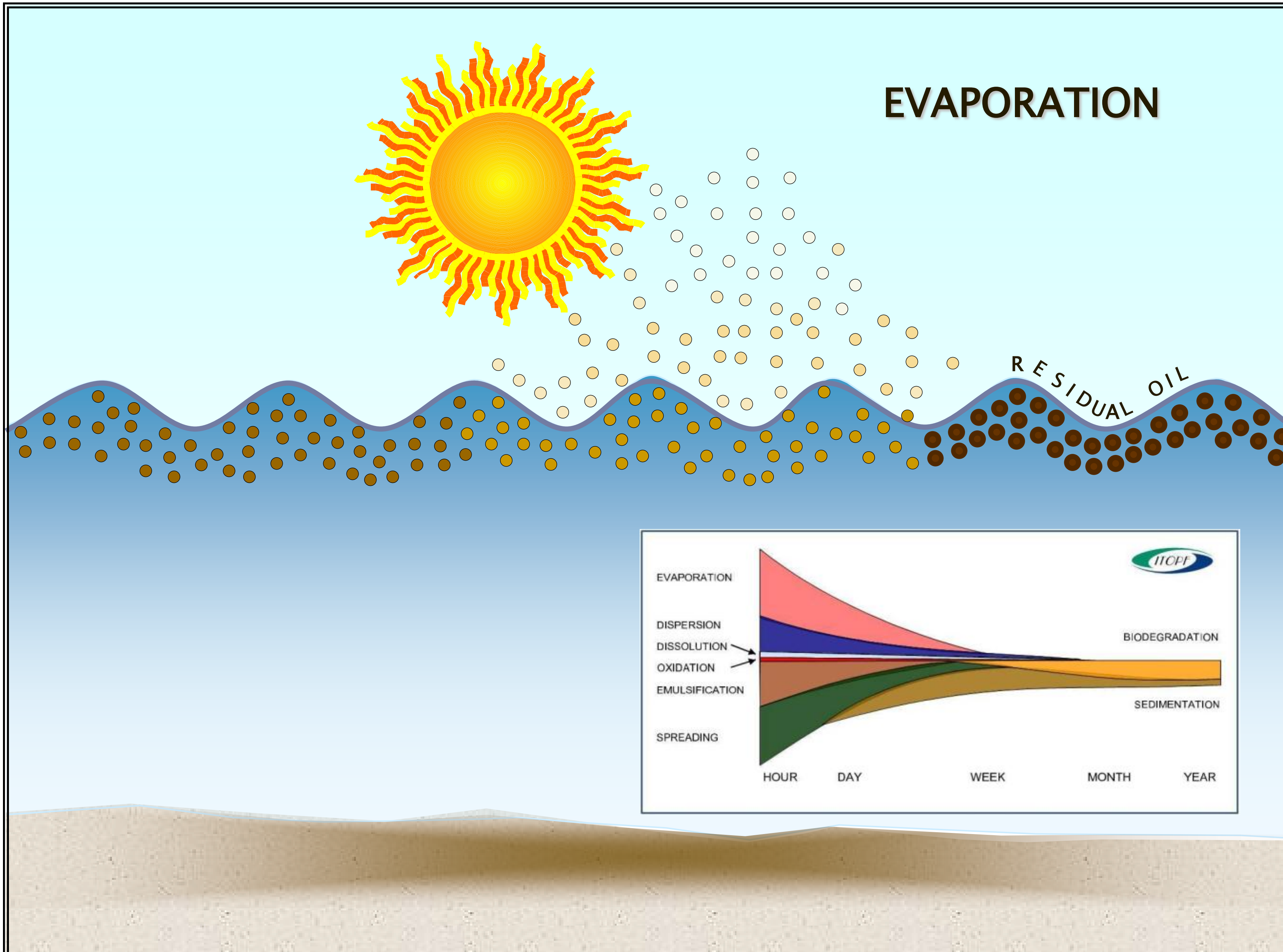
- Spreading
- Evaporation
- Dispersion
- Dissolution
- Oxidation
- Emulsification
- Sedimentation
- Microbial Degradation

Relationship Between Thickness and Color for Oil on Water



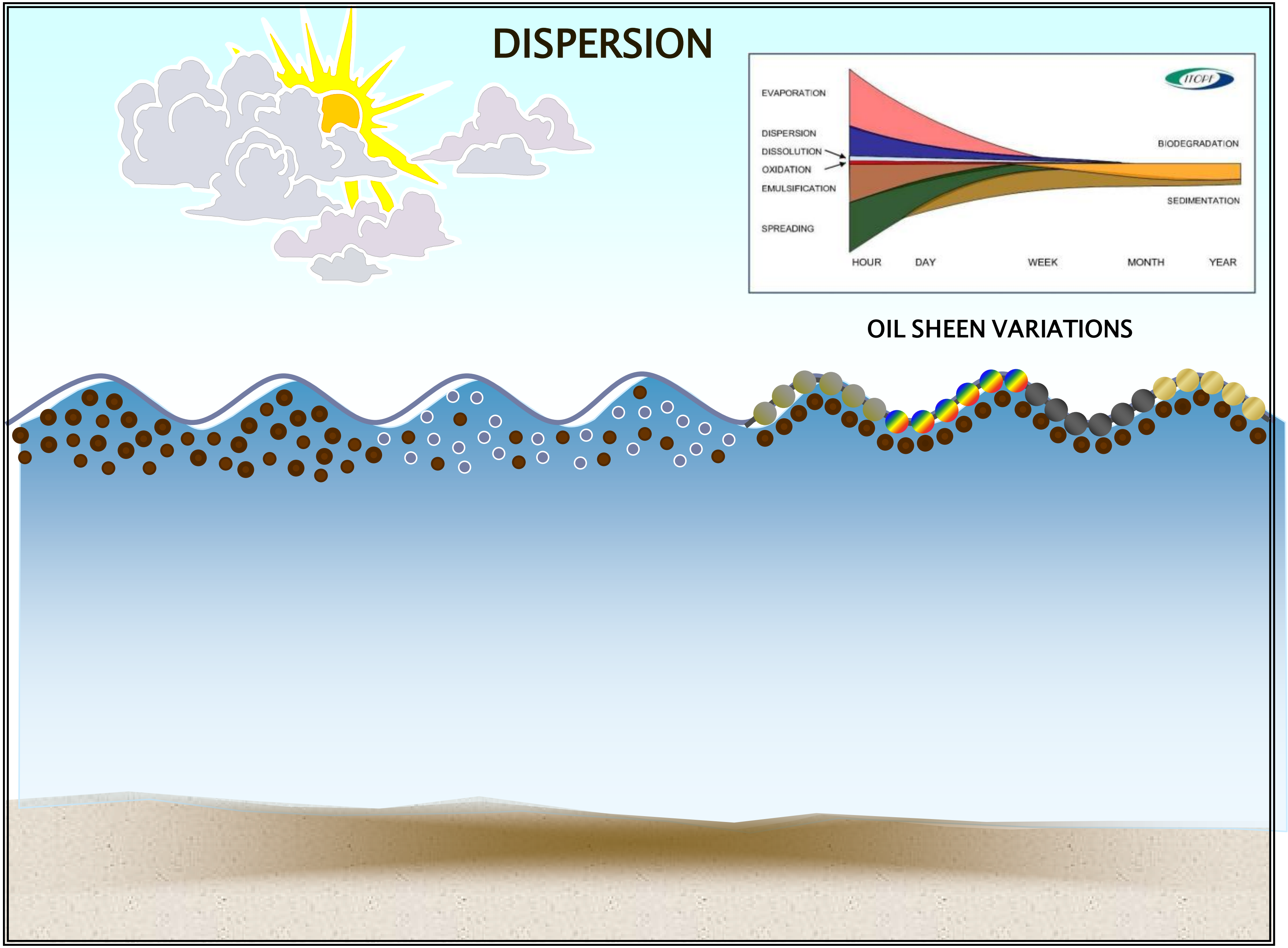
Spreading

- Consequence of gravity and physics (liquid on a liquid)
- Function of: oil properties, environmental factors
  - Viscosity – higher V = less spreading
  - Pour Point – below pour point = less spreading
  - Higher energy (current velocity, wind etc.) = MORE spreading
- Over time more spreading, results in sheen


EVAPORATION
RESIDUAL OIL
EVAPORATION
DISPERSION
DISSOLUTION
OXIDATION
EMULSIFICATION
SPREADING
BIODEGRADATION
SEDIMENTATION
HOUR
DAY
WEEK
MONTH
YEAR
ITOPF

Evaporation

- Loss light fractions from liquid to the surrounding atmosphere
- Function of: oil type, environmental factors
  - Crude oil - up to % loss in 24 hours? **25**
  - Gasoline - up to % loss in 10 minutes? **50**
  - No. 6 fuel oil –% loss in 40 hours? **5-10**
- Over time less evaporation, and more “oil residue” which has higher viscosity and higher specific gravity than original oil


DISPERSION
EVAPORATION
DISPERSION
DISSOLUTION
OXIDATION
EMULSIFICATION
SPREADING
BIODEGRADATION
SEDIMENTATION
HOUR
DAY
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YEAR
OIL SHEEN VARIATIONS

Dispersion

- Other major "removal" mechanism
- Decreases as viscosity increases
- Droplets 50-70 microns in diameter are not likely to resurface due to turbulence

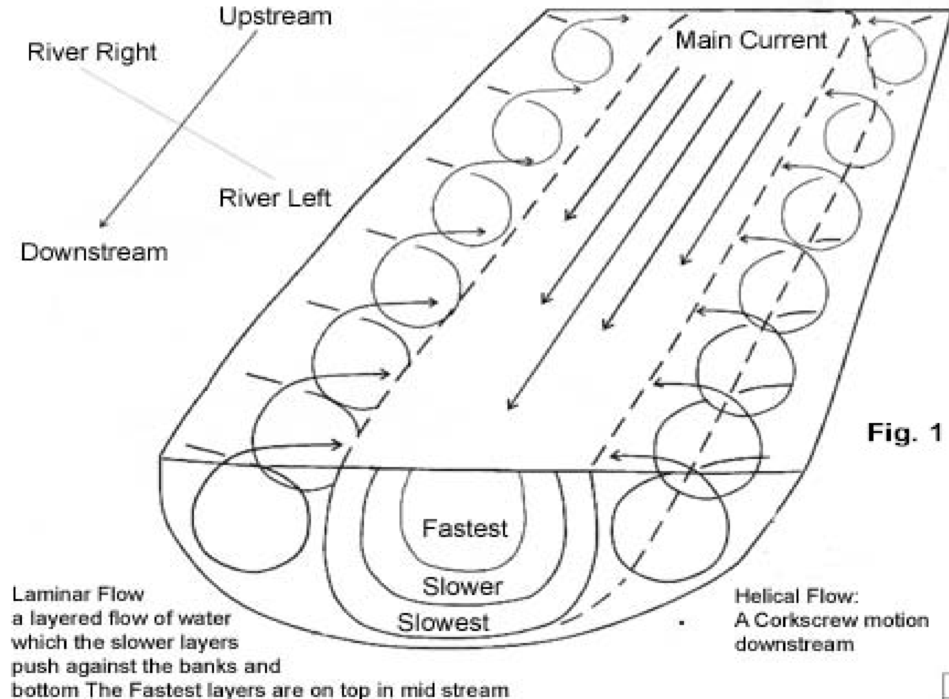
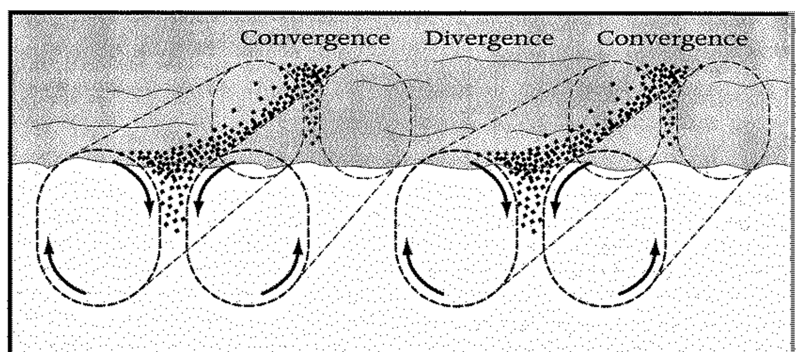
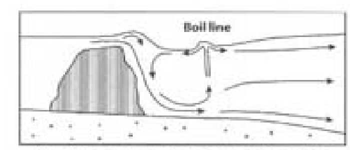
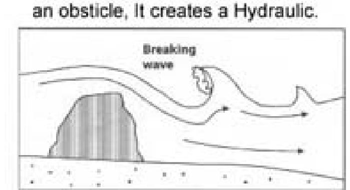


Fig. 1

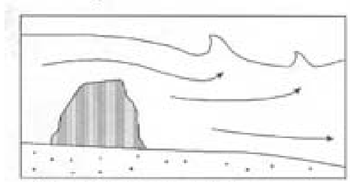




As Water level rises and flows over an obsticle, It creates a Hydraulic.



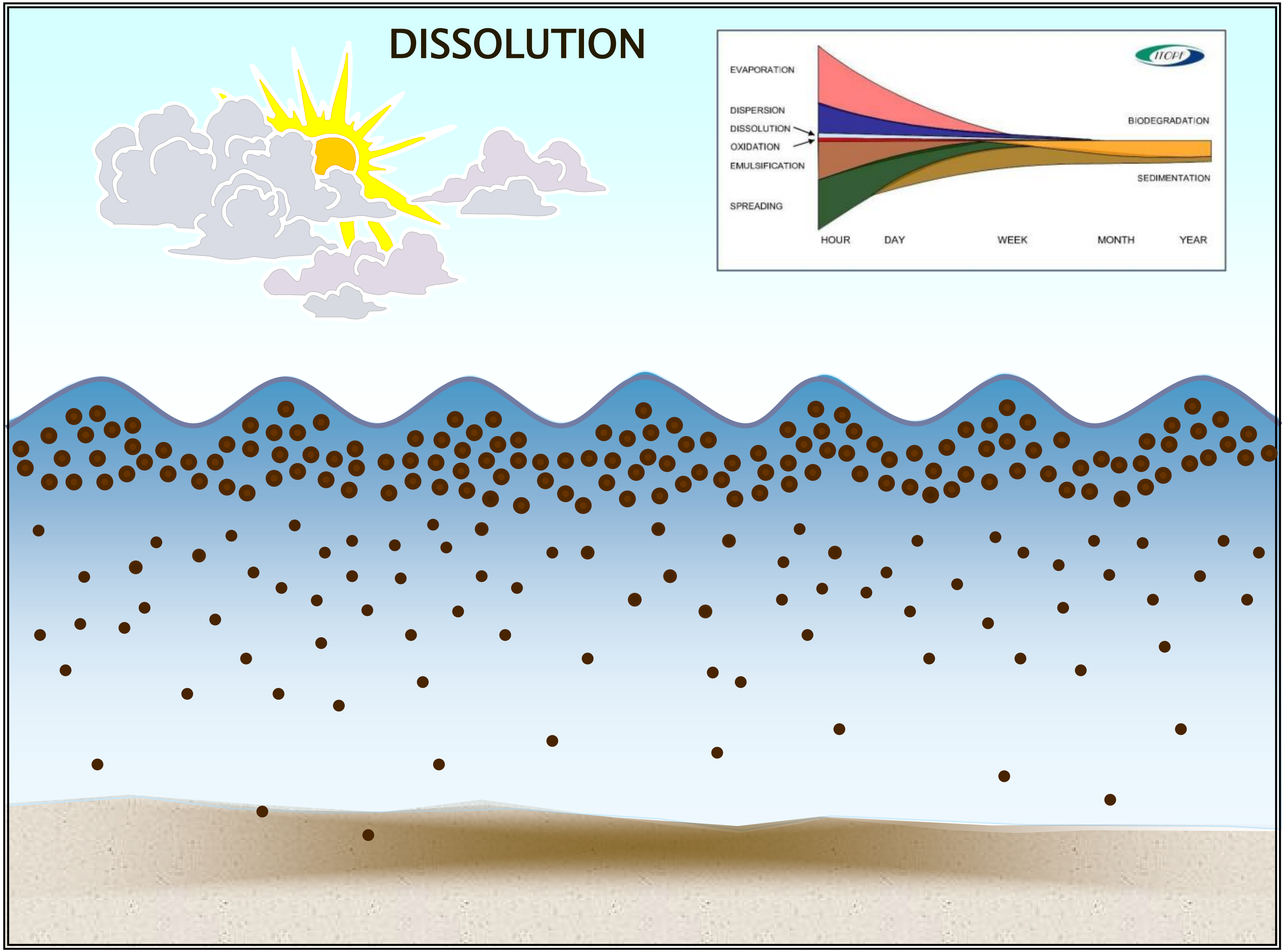
As the current deepens, it forms breaking waves or holes.



As the water deepens still more, the waves become smaller and stop breaking

Which one is dispersion a greater factor?

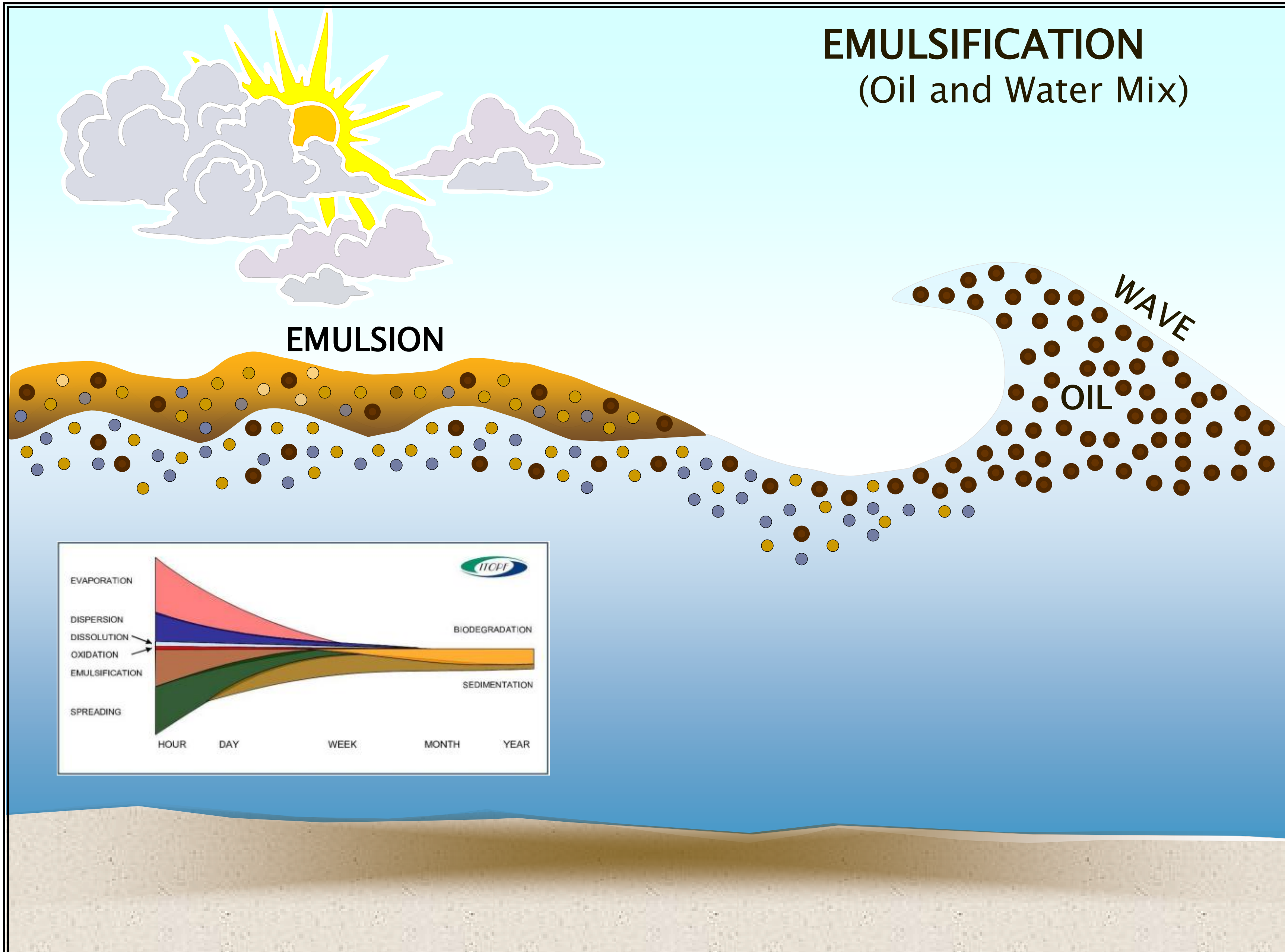
DISSOLUTION



Dissolution

- Less than 0.1% (very heavy oil) to 2% (gasoline) of the spilled oil (Hydrocarbons) volume actually dissolves into the water column
- However, sulfur compounds and salts common to crude oils will be lost to dissolution
- Dissolution is a long term process, and continues as oxidation and biodegration produce additional soluble compounds

What is more toxic to aquatic biota– gasoline or No. 6 fuel oil? WHY?


EMULSIFICATION
(Oil and Water Mix)
EMULSION
WAVE
OIL
EVAPORATION
DISPERSION
DISSOLUTION
OXIDATION
EMULSIFICATION
SPREADING
BIODEGRADATION
SEDIMENTATION
HOUR
DAY
WEEK
MONTH
YEAR

Emulsification

- Emulsification is the process by which one liquid is dispersed into another liquid in the form of small droplets
- Requires **energy** such as swift current or wave action (ex situ)
- Can occur downhole (in situ) in the formation and during production/recovery

Water-in-oil emulsification

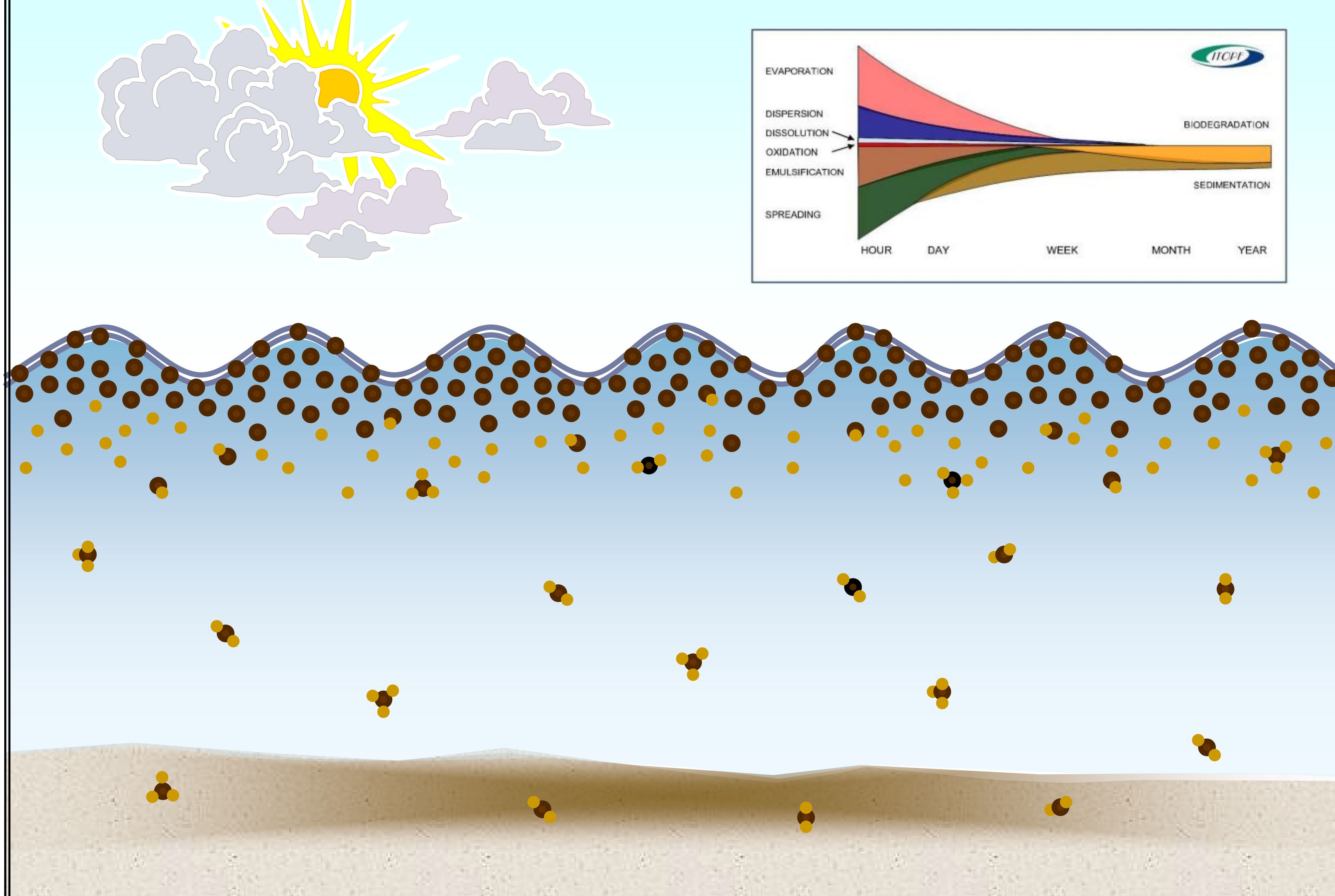
- Butter is an example of Water-in-oil emulsification
- Extremely stable emulsion, may persist for months or years
- 30-50% water - flow freely
- 50-80% water - brown, grease-like "chocolate mousse"
- High viscosity, high specific gravity oils tend to form "chocolate mousse"
- Further weathering of "chocolate mousse" is extremely slow
- "Chocolate mousse" tends to pick up sand and debris and once water evaporates, forms compact tarry lumps


mousse


NOT
mousse


pollen

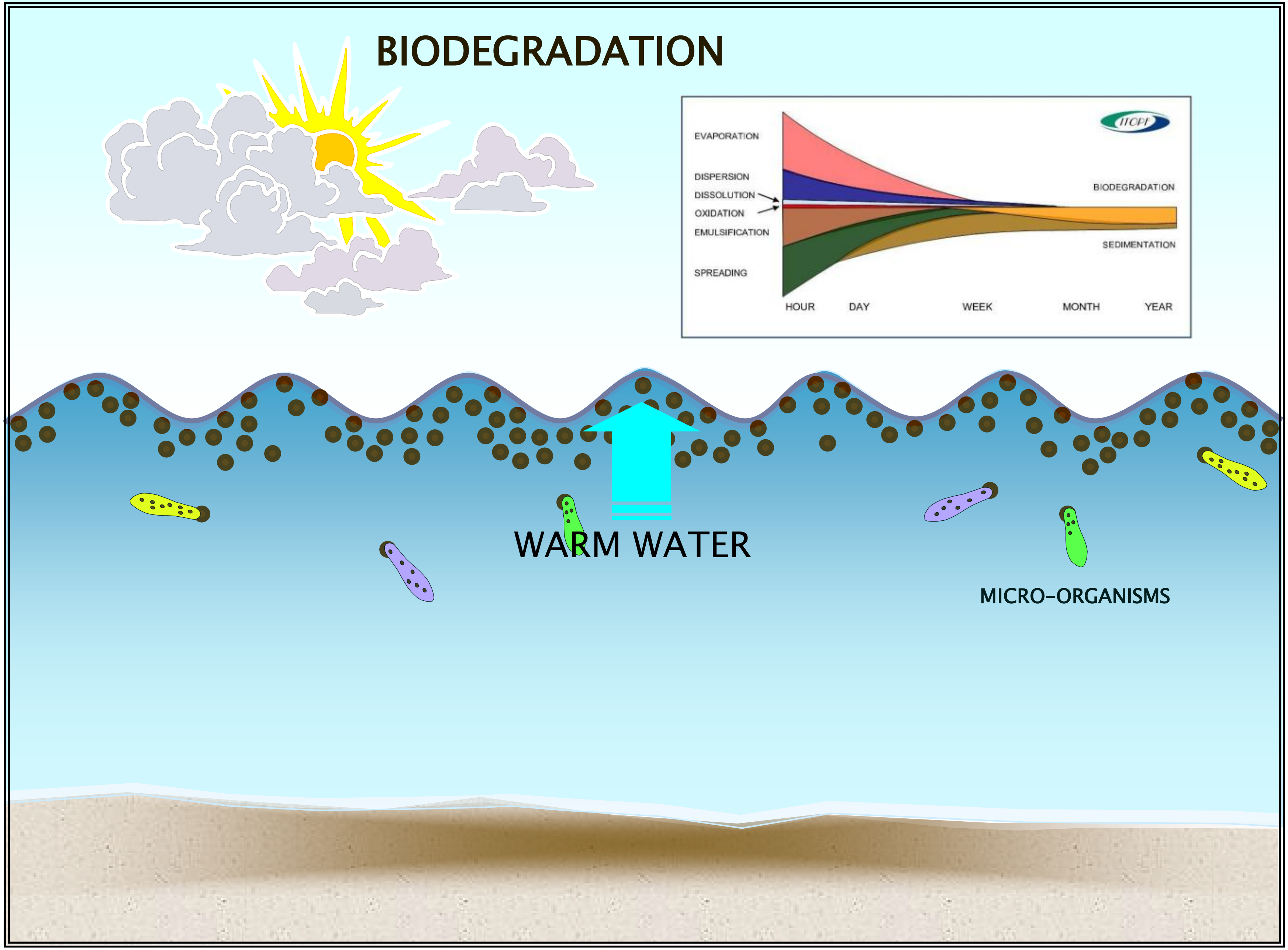
SEDIMENTATION



Sedimentation

- Adhesion of oil to solid particles in the water column
- Mostly occurs in muddy rivers, streams
- Can occur when oil/sand mix in turbulent rivers

A) 10,000 g/m^3
B) 1000 g/m^3
C) 100 g/m^3
D) 10 g/m^3
E) 1 g/m^3


BIODEGRADATION
EVAPORATION
DISPERSION
DISSOLUTION
OXIDATION
EMULSIFICATION
SPREADING
BIODEGRADATION
SEDIMENTATION
HOUR
DAY
WEEK
MONTH
YEAR
ITOPF
WARM WATER
MICRO-ORGANISMS

Biodegradation

- Oil degrading microbes are present in all aquatic environments to some extent
- Ultimate fate of most oil spilled into the environment
- Controlled by:
  - Nutrients/Oxygen
  - Temperature
  - Oil composition
  - Bioavailability

Behavior in the Environment

- Spreading of the oil and weathering of oil depends on the *type of oil* and the *environmental conditions*
- Spreading on water affected by *wind, water currents, force of gravity and surface tension*
- High Viscosity and high pour point can limit? *spreading*

Movement of an Oil Slick

- Water Current and Wind predominantly affect movement of oil slicks
- However, strong winds may move a slick “up current”
- Winds in excess of 10 MPH may cause the slick to break up into streaks or windrows
- Can be difficult to predict the movement of oil on water

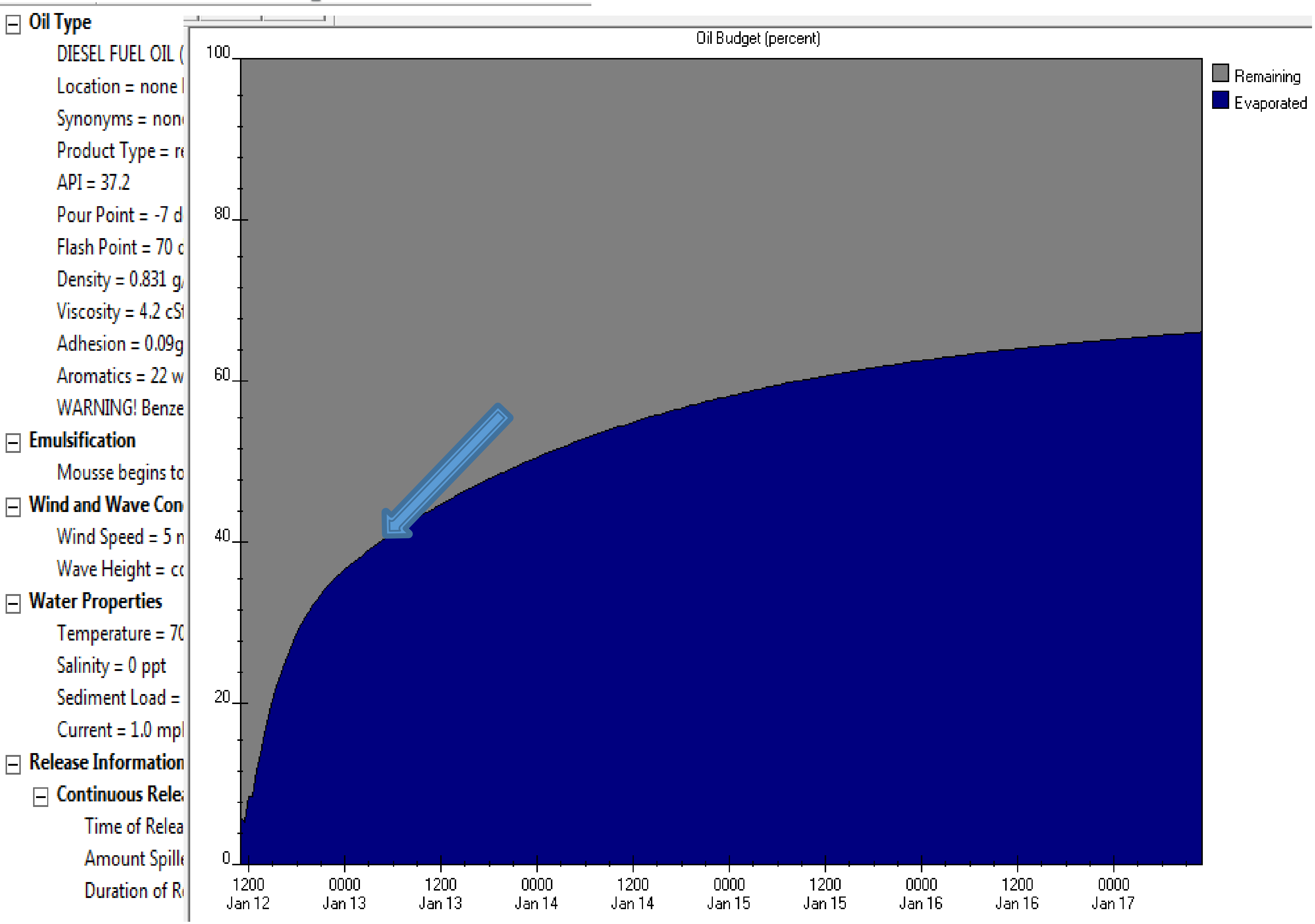
SUMMARY

- Oil is a varied substance.
- The properties of oil effect ***fate*** and ***transport***.
- The properties, extent and fate of oil changes as it weathers.
- Knowing the properties of oil and the nature of oil weathering is critical to making sound response decisions.

Activity– Using Adios

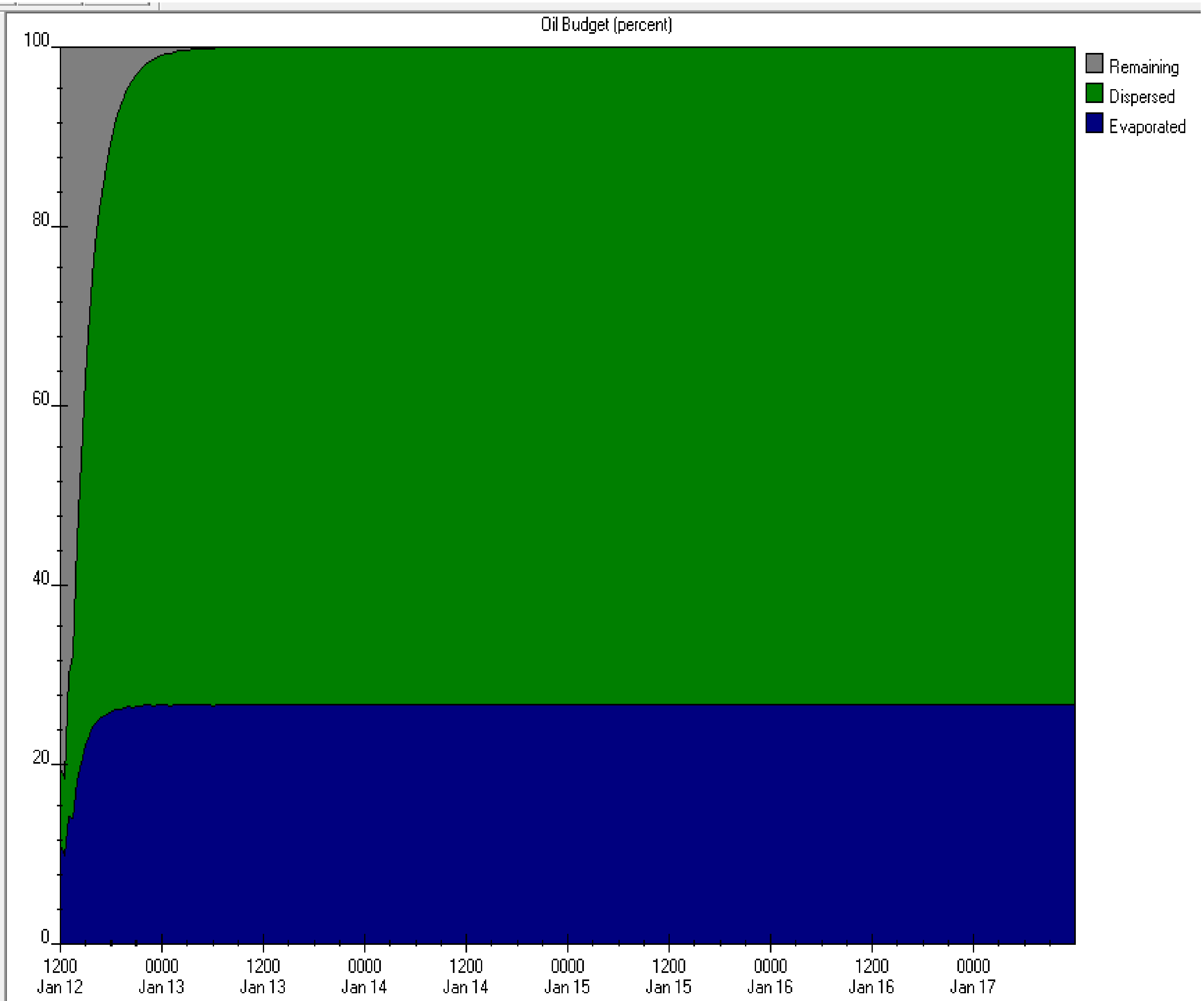
- Adios is a tool designed to predict oil weathering.
- Primarily designed for ***open water***
- Offers some value to confined water in streams and more confined water bodies

Example 1– Diesel fuel oil



Example 2– Diesel fuel oil

- Oil Type
  - DIESEL FUEL (
  - Location = nc
  - Synonyms = r
  - Product Type
  - API = 37.2
  - Pour Point = ·
  - Flash Point =
  - Density = 0.83
  - Viscosity = 4.2
  - Adhesion = 0.
  - Aromatics = 2
  - WARNING! Be
- Emulsification
  - Mousse begir
- Wind and Wave (
  - Wind Speed =
  - Wave Height
- Water Propertie
  - Temperature
  - Salinity = 0 pp
  - Sediment Loa
  - Current = 1.0
- Release Informa
  - Continuous R
    - Time of R
    - Amount S
    - Duration (

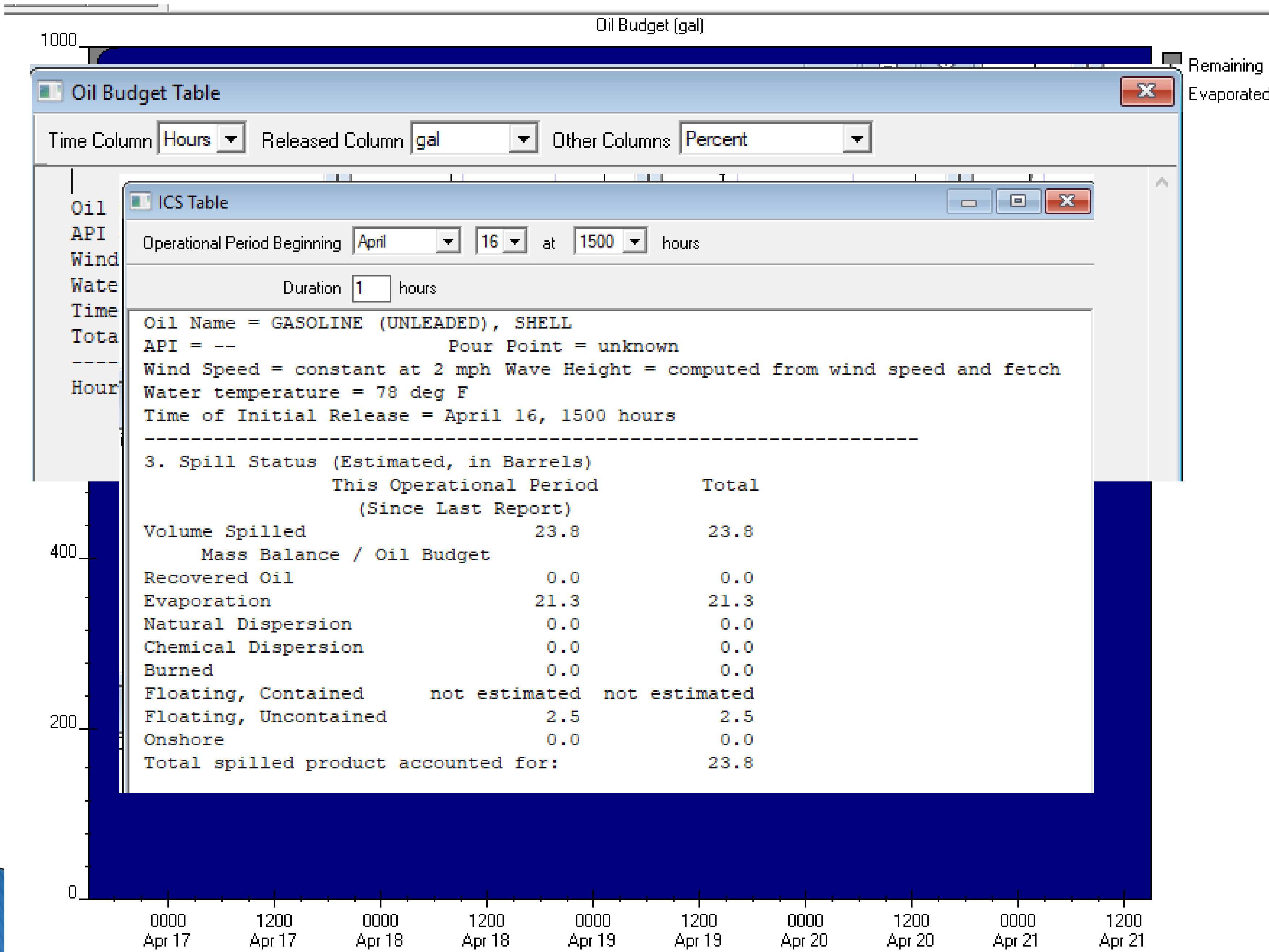


Using Adios for Inland Waters

- Be careful when making inputs into Adios
  - Name of oil matters, watch out for “oil name”
  - Be careful about entering **wind** conditions for “closed waters”–Adios is designed to allow for uninhibited spreading and calculates wave height based on wind speed
- May be able to find surrogates for your oil based on oil properties (API, viscosity, etc.)
- Consult your friendly SSC for assistance

Adios Activity

- Gasoline spill- 1000-2000 gallons
- How much remains after 1 hour in open water?


Oil Budget (gal)
1000
400
200
0
Remaining
Evaporated
0000 Apr 17
1200 Apr 17
0000 Apr 18
1200 Apr 18
0000 Apr 19
1200 Apr 19
0000 Apr 20
1200 Apr 20
0000 Apr 21
1200 Apr 21
Oil Budget Table
Time Column Hours
Released Column gal
Other Columns Percent
Oil
API
Wind
Wate
Time
Tota
Hour
ICS Table
Operational Period Beginning April 16 at 1500 hours
Duration 1 hours
Oil Name = GASOLINE (UNLEADED), SHELL
API = -- Pour Point = unknown
Wind Speed = constant at 2 mph Wave Height = computed from wind speed and fetch
Water temperature = 78 deg F
Time of Initial Release = April 16, 1500 hours
3. Spill Status (Estimated, in Barrels)
This Operational Period (Since Last Report) Total
Volume Spilled 23.8 23.8
Mass Balance / Oil Budget
Recovered Oil 0.0 0.0
Evaporation 21.3 21.3
Natural Dispersion 0.0 0.0
Chemical Dispersion 0.0 0.0
Burned 0.0 0.0
Floating, Contained not estimated not estimated
Floating, Uncontained 2.5 2.5
Onshore 0.0 0.0
Total spilled product accounted for: 23.8