Tuzzy Talk 2:
What Happens When Crude Oil Gets into Water?

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Today's Topics

- **Goals of This Series**
- **Review of Last Week: What Is Crude Oil Anyway?**
- **This Week: What Happens When Crude Oil Gets Into Water?**
  - **Not Human Intervention (spill response)**
  - **Natural Processes (Fate and Behavior of Oil in Water)**

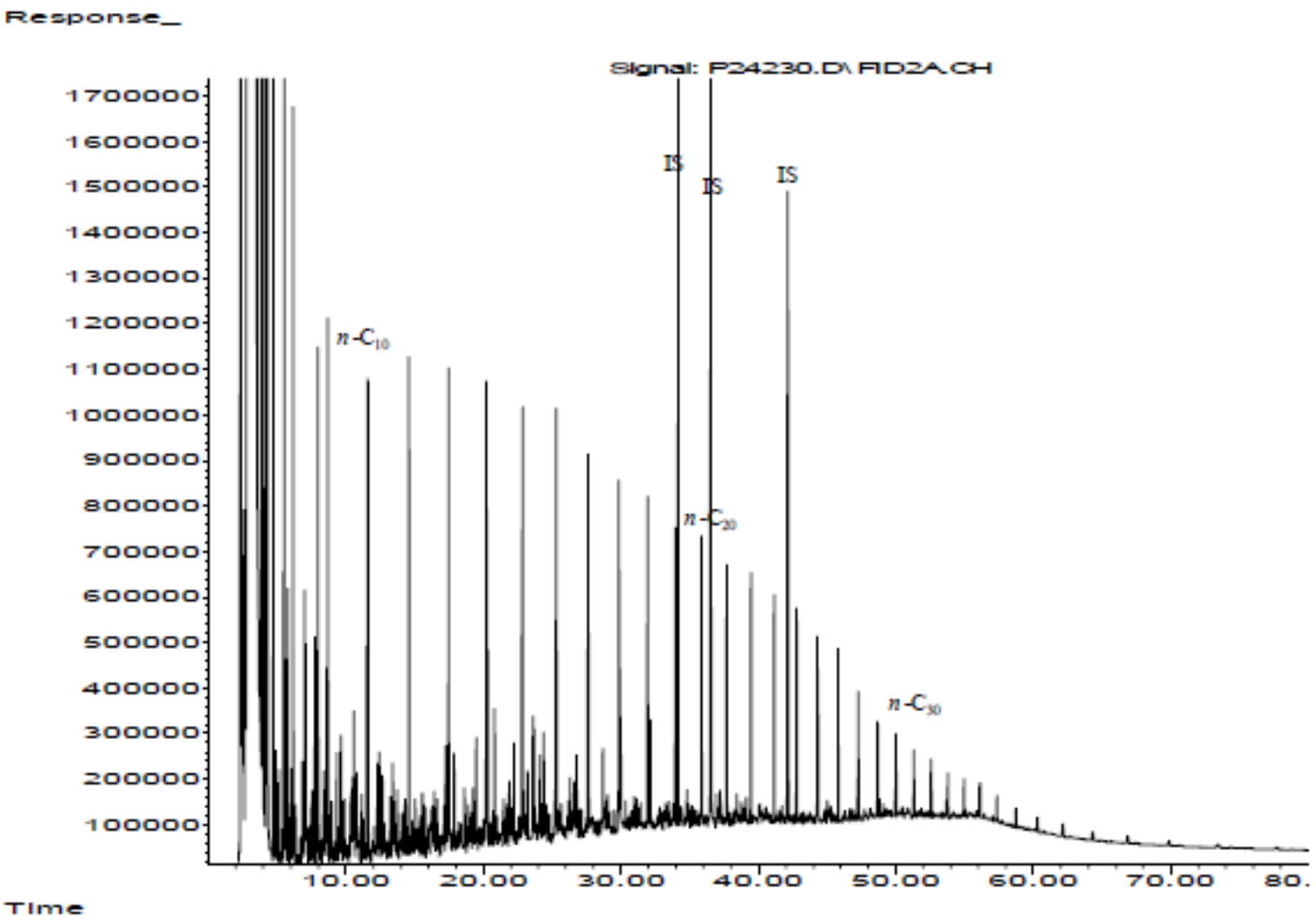
Review of Last Week
Crude Oil Characteristics

(Crude oils vary from place to place and over time from the same place)

Crude Oil Is Made of Hundreds of Chemical Compounds:

All Contain Carbon (C) and Hydrogen (H) (Hydrocarbons)

Figure 3. GC/FID chromatogram of North Slope crude oil.

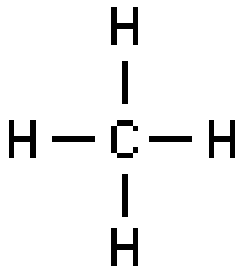


30% Crude Oil = Paraffins (Single Bonds Between Carbons in Molecule and Arranged in Lines)

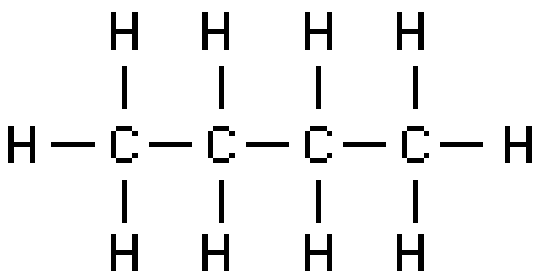
Methane is the simplest paraffin molecule:

Examples of straight chain paraffin molecule (Butane) and branched paraffin molecule (Isobutane) with same chemical formula of:

Methane (CH_4)



Butane (C_4H_{10})



Isobutane (C_4H_{10})

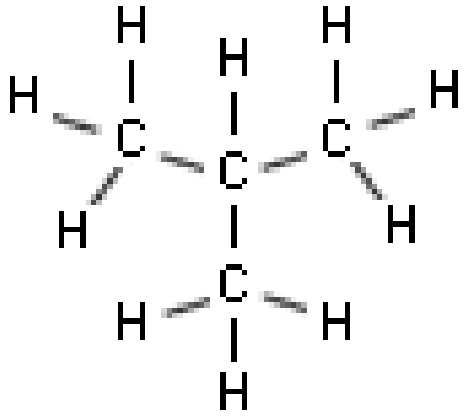
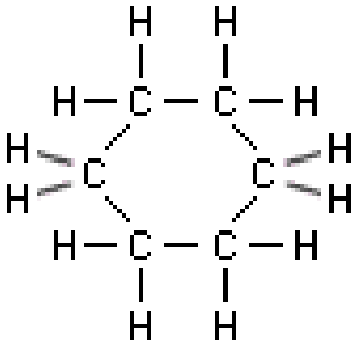


Figure 1: Typical paraffins

49% Crude Oil = Naphthenes (Single Bonds Between Carbons in Molecule, But Arranged in Ring)

Example of a typical single-ring naphthenic:

Cyclohexane



Example of naphthene with same chemical formula (C_6H_{12}) but with a different molecular structure:

Methylcyclopentane (C_6H_{12})

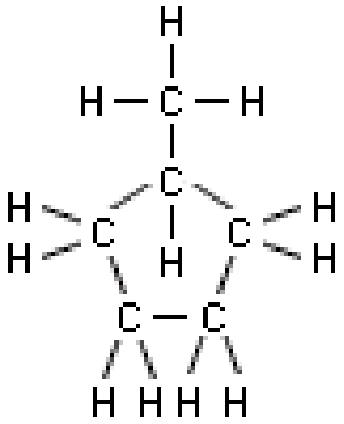
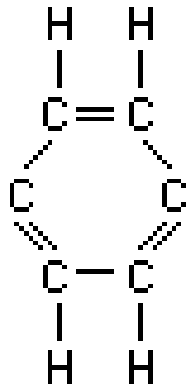


Figure 3: Typical naphthenes

15% Crude Oil = Aromatics (Double Bonds Between Carbons in Molecule, And Arranged in Ring)

Example of simple aromatic compound:

Benzene (C_6H_6)



Example of simple double-ring aromatic compound:

Naphthalene ($C_{10}H_8$)

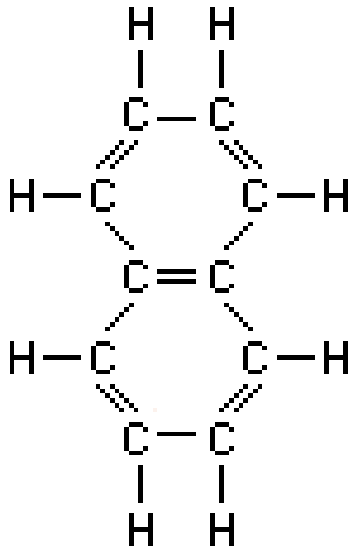
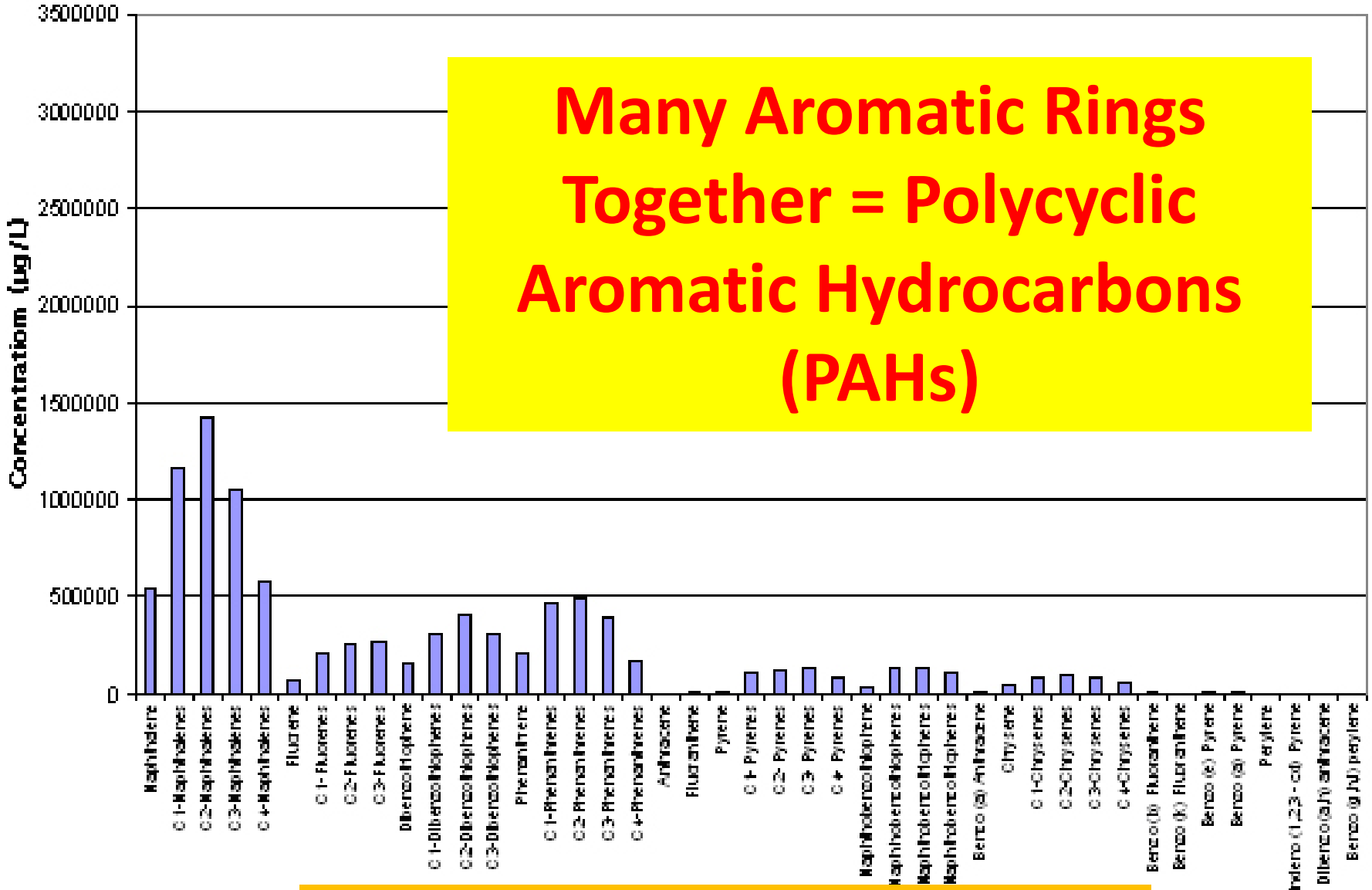


Figure 2: Typical aromatics



PAHs in North Slope Crude

Density

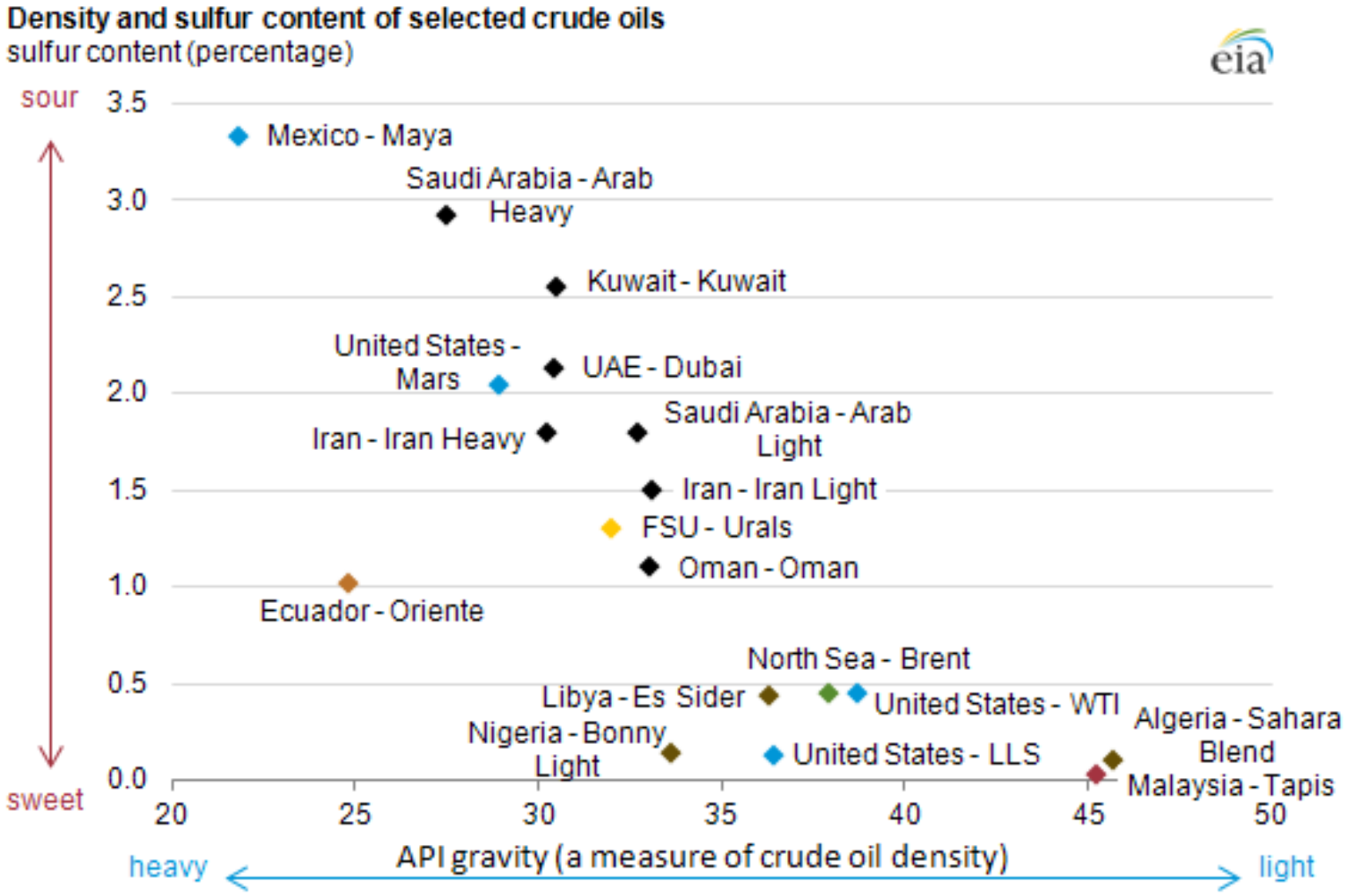
- **Mass of Substance per Volume**
  - **1 mL water has a mass of approximately 1 gram**
  - **(5 ml = 1 teaspoon)**
  - **Density of crude oil varies from 0.8 to 0.9+ g/mL**
  - **Lower temperature = Higher density**
  - **For water: Higher salinity = Higher density**

Specific Gravity

- **Specific Gravity = $\frac{\text{Density of Oil}}{\text{Density of Water}}$**
- **SG less than 1 means oil floats on water**
- **This in the usual case!**

API Gravity

- **API Gravity = $\frac{141.5}{SG}$ - 131.5**
- **API Gravity Less than 10, Oil Sinks**
- **API Gravity Close to 1, Could Float or Sink**
  - **Depends on particles in water, etc.**
- **API Gravity Greater than 10, Oil Floats**



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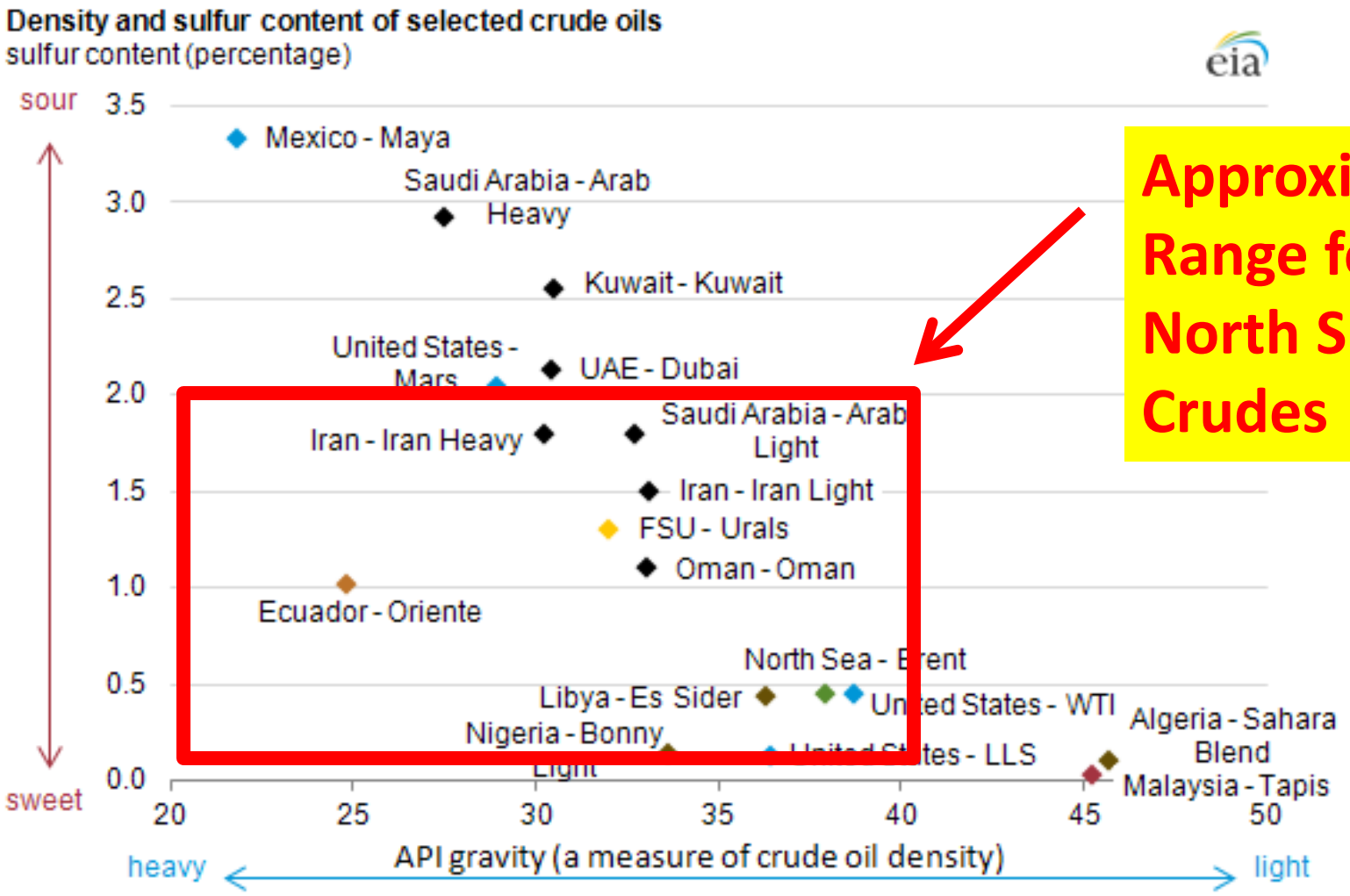
Notes: Points on the graph are labeled by country and benchmark name and are color coded to correspond with regions in the map below. The graph does not indicate price or volume output values. United States-Mars is an offshore drilling site in the Gulf of Mexico. WTI = West Texas Intermediate; LLS = Louisiana Light Sweet; FSU = Former Soviet Union; UAE = United Arab



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Notes: Points on the graph are labeled by country and benchmark name and are color coded to correspond with regions in the map below. The graph does not indicate price or volume output values. United States-Mars is an offshore drilling site in the Gulf of Mexico. WTI = West Texas Intermediate; LLS = Louisiana Light Sweet; FSU = Former Soviet Union; UAE = United Arab

Viscosity

- Resistance of fluid to moving (does it flow easily?)
  - Water pretty mobile, flows well
  - Honey and molasses less mobile (higher viscosity)
  - Viscosity of oil in between these extremes
- Colder temperatures increase viscosity

Volatility

- **Desire to go into air**
  - **More volatile = More Preference for Air**
- **Function of Boiling Point of Compounds in Oil**
- **Fewer Carbons in Compound = More Volatile**
- **Volatile Compounds Evaporate into Air**

Solubility

- Desire to Dissolve into Water
- Though Most Compounds in Oil Do Not Dissolve Well in Water, They Do Dissolve to some Extent
  - Sugar Solubility in Water ~ 1 lb per cup water (Room Temp)
  - Crude Oil Compounds ~ 1 lb oil per 200 to 200 million gallons of water
    - (1 ug/L to 1000mg/L)
- Temperature Affects Solubility

What Happens When Crude Oil Gets Into Water?

Natural Processes (Fate and Behavior of Oil in Water)

Topics Today

- Surface Oil Slicks Only
  - Most spills create surface oil slicks
  - Oil Floats on Water
    - Density, Specific Gravity, API Gravity All Show This

- **No Subsurface Releases Today**
  - **More Complicated, But Usually Some Floats to Surface**

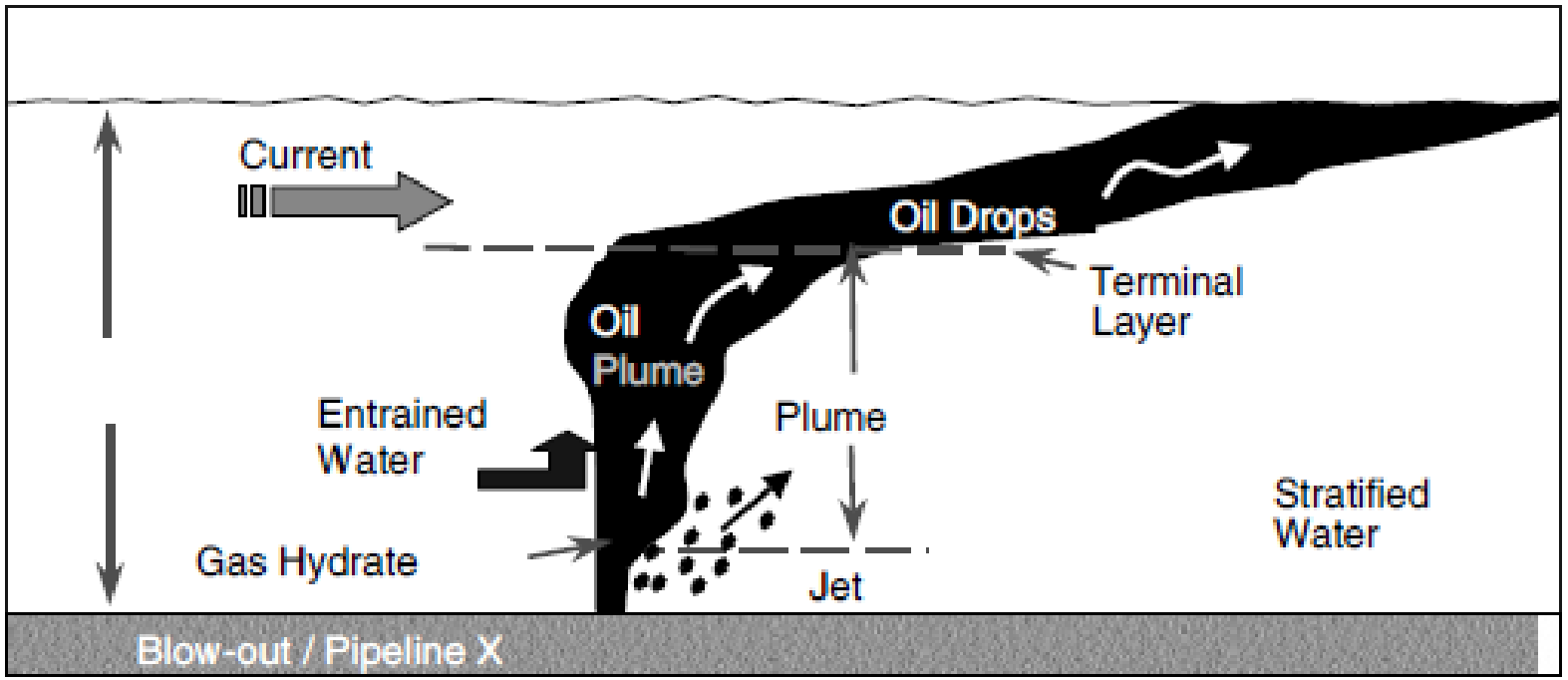
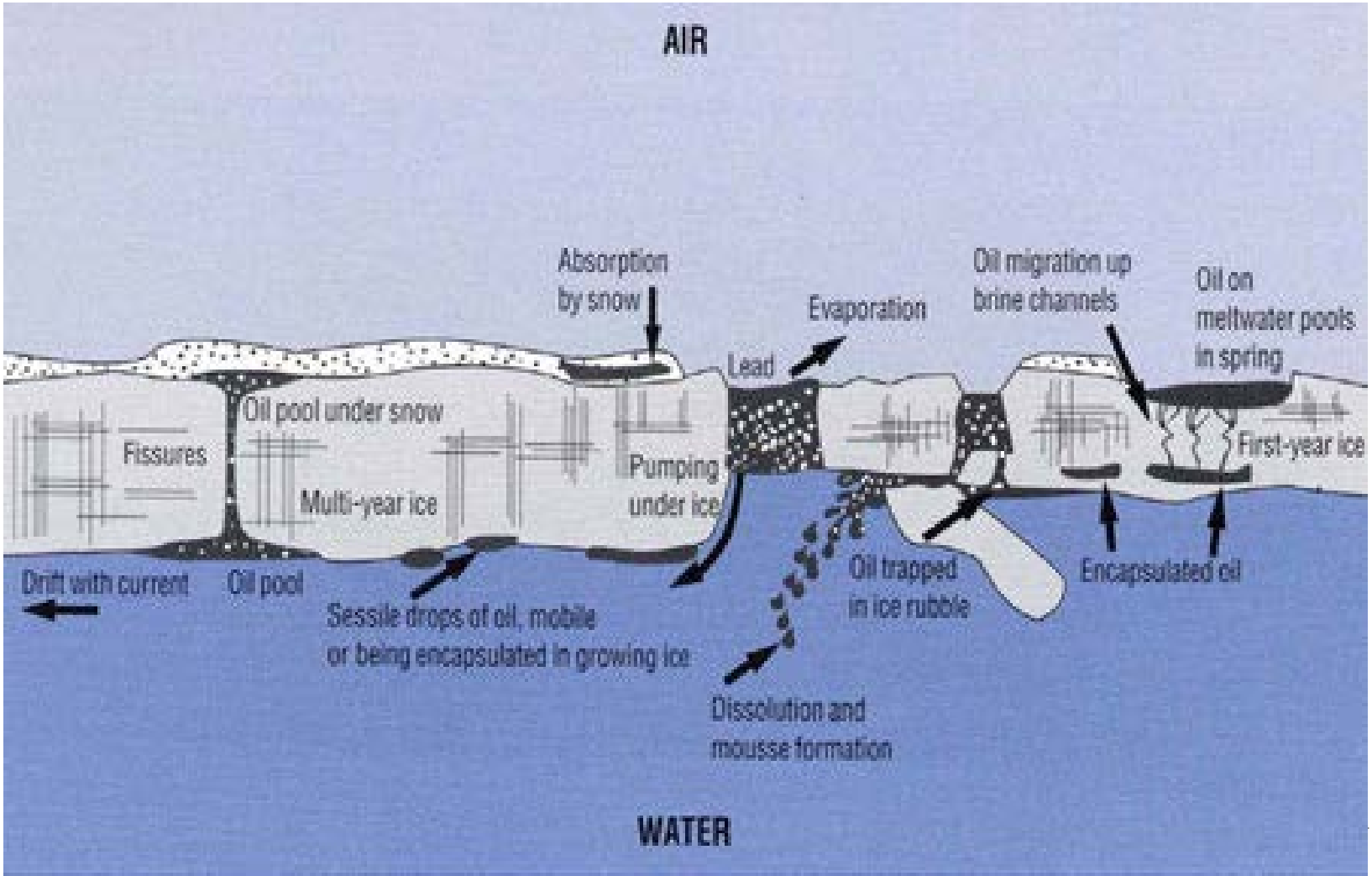


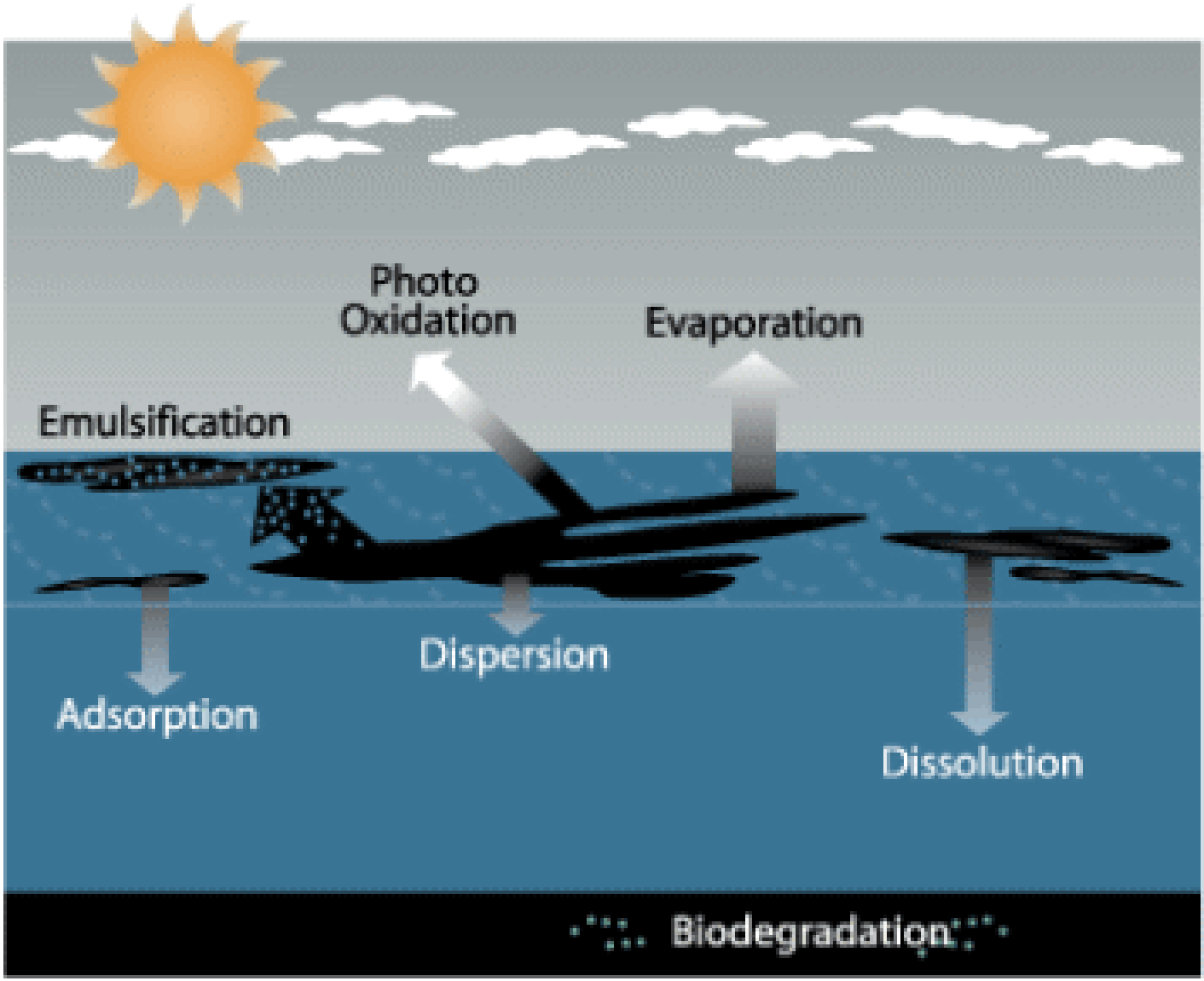
FIGURE 4-6 Schematic diagram depicting the basic physical processes involved in a deepwater subsurface oil and gas release.

- **No Ice Today, It Complicates Where/How Oil Moves**
  - **Oil Floats in Leads**



What Happens When Crude Oil Gets Into Water?

Natural Processes (Fate and Behavior of Oil in Water)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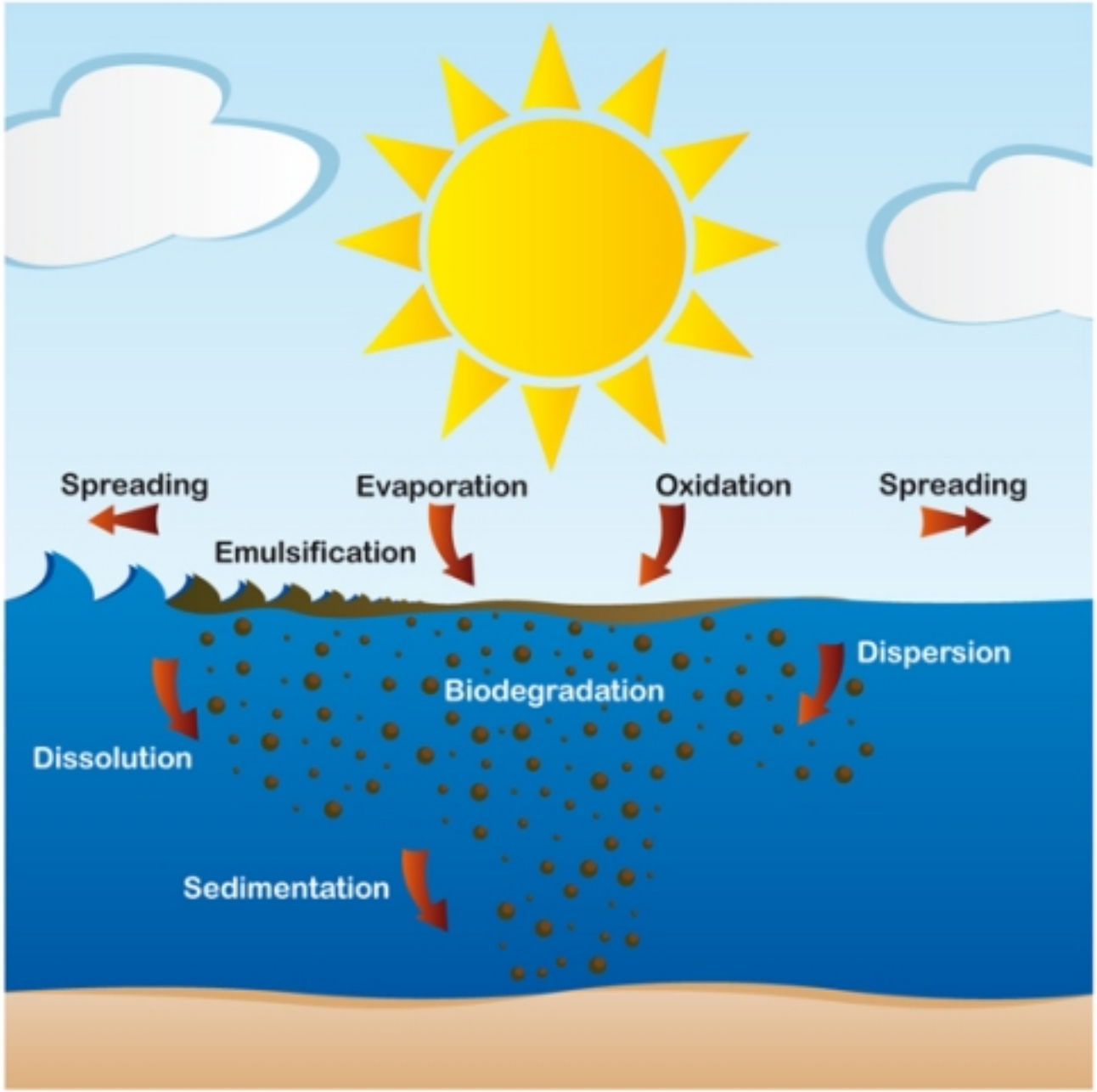
Evaporation
Emulsification
Dispersion
Adsorption
Dissolution
Biodegradation


Spreading
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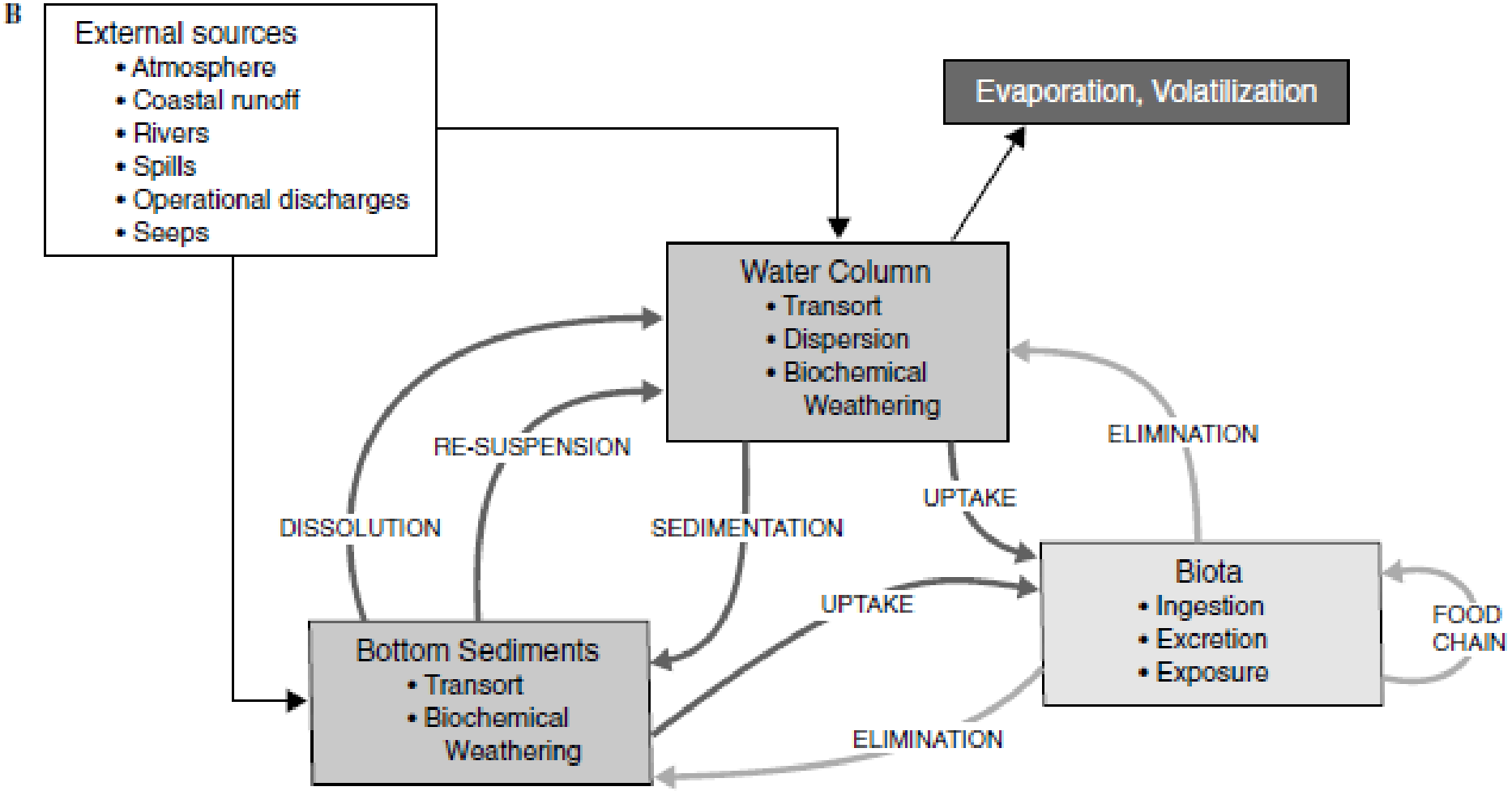
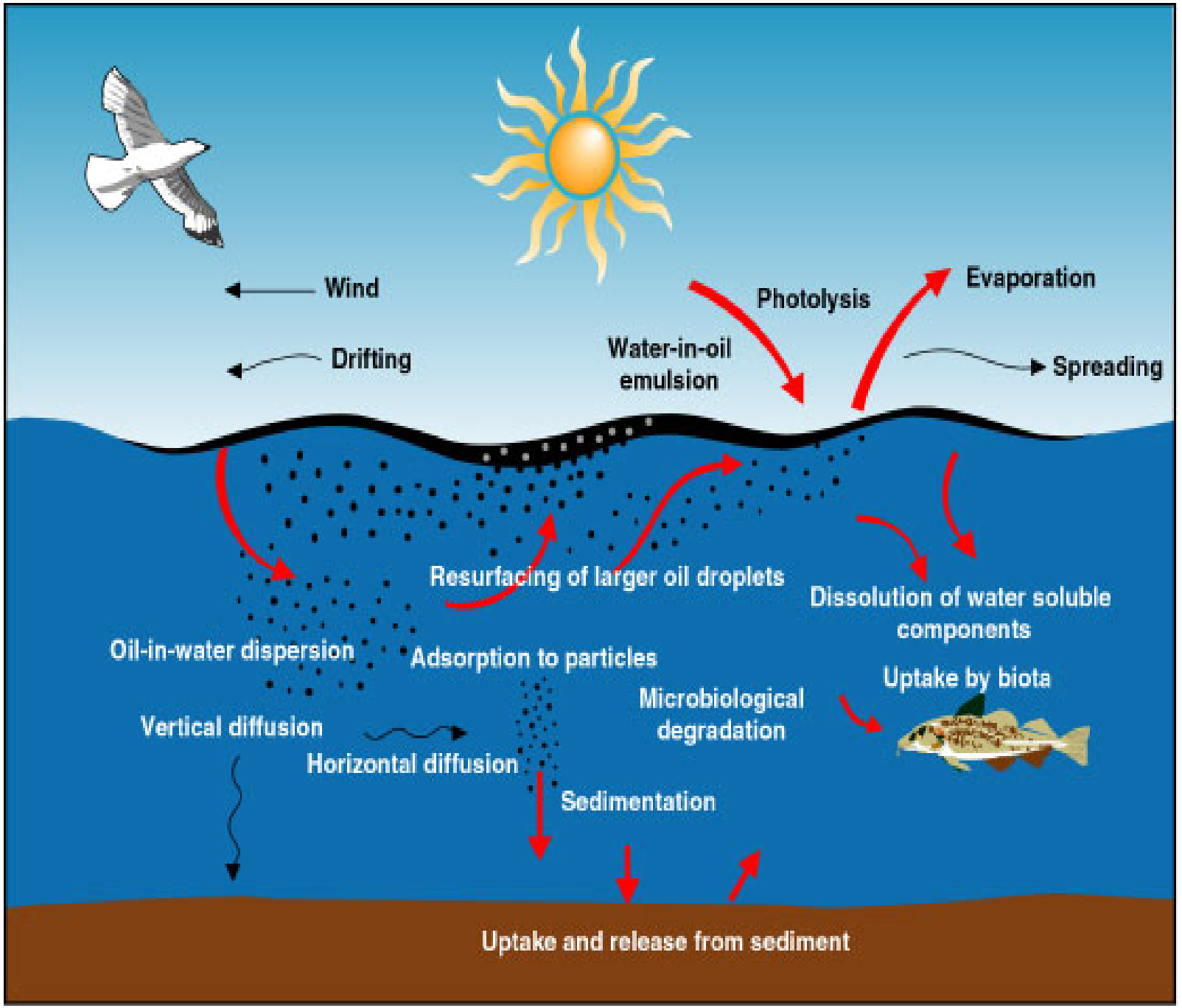
Dissolution
Sedimentation


B
External sources
• Atmosphere
• Coastal runoff
• Rivers
• Spills
• Operational discharges
• Seeps
Evaporation, Volatilization
Water Column
• Transort
• Dispersion
• Biochemical Weathering
RE-SUSPENSION
DISSOLUTION
SEDIMENTATION
UPTAKE
ELIMINATION
Biota
• Ingestion
• Excretion
• Exposure
FOOD CHAIN
UPTAKE
Bottom Sediments
• Transort
• Biochemical Weathering
ELIMINATION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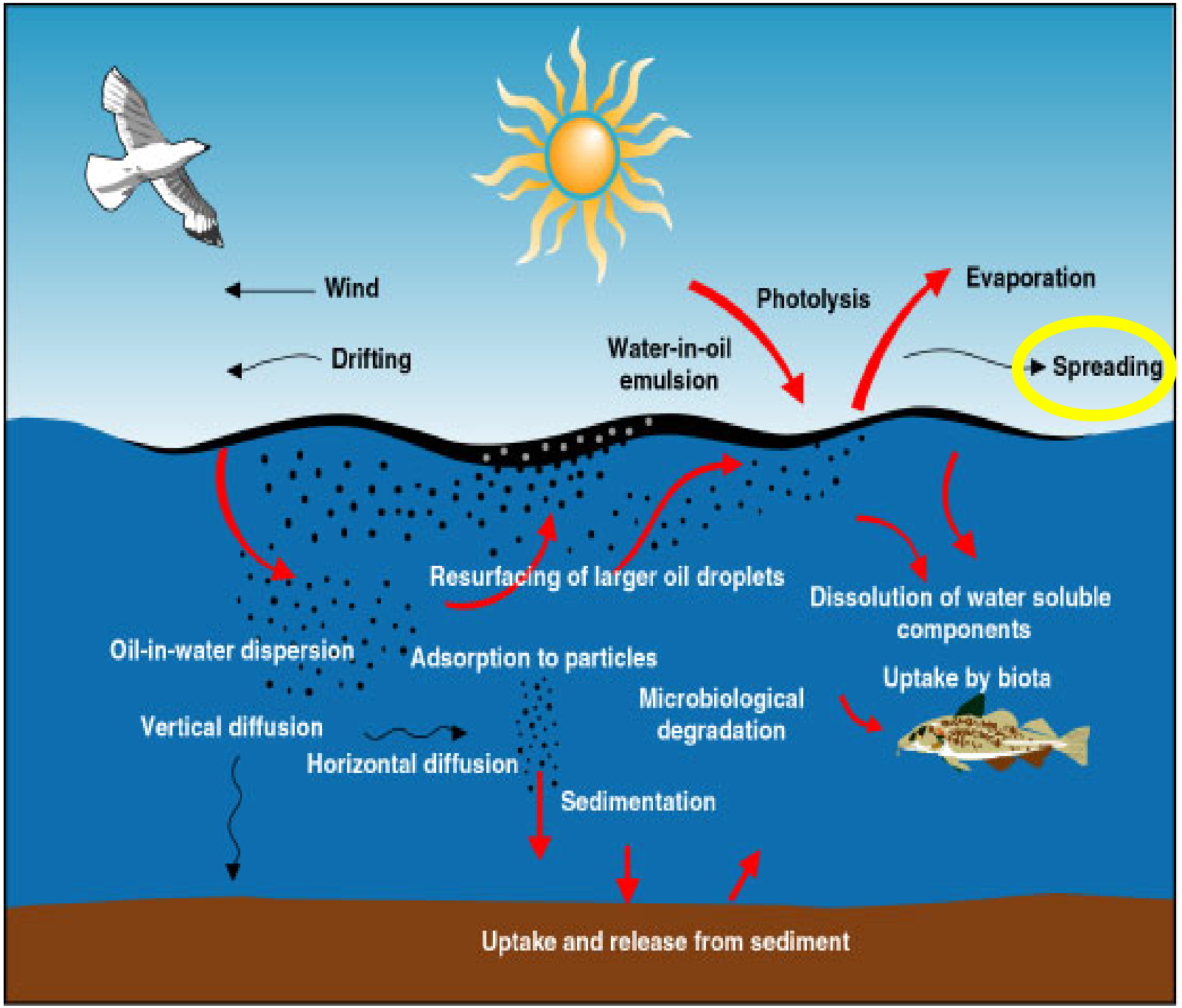
Uptake and release from sediment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Spreading

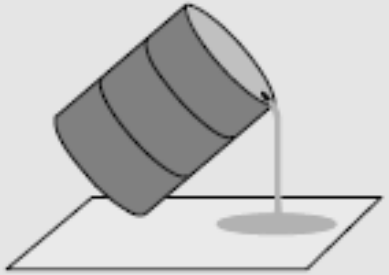
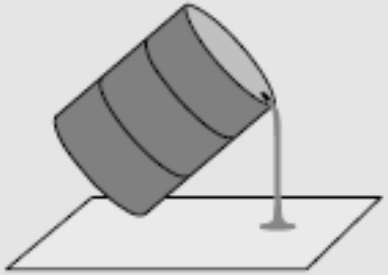
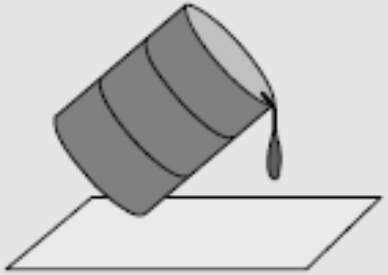
- **Fay's Simplified Calculation (Circular)**

  Max. Radius (ft)= 72.5 x (Vol in gallons)$^{0.375}$

  Area (ft^2) = 16,500 x (Vol in gallons)$^{0.75}$

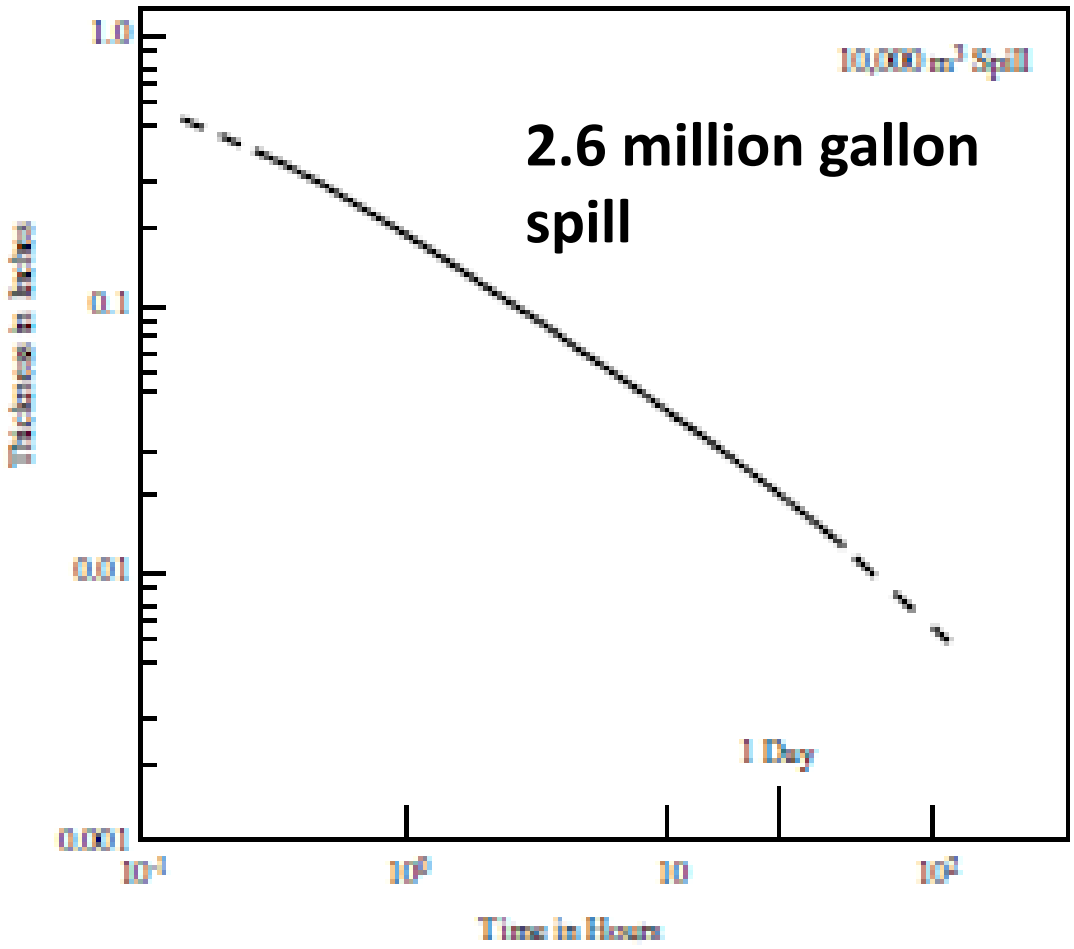
- **Wind and Waves Distort Spreading from Circular Shape and Break It into Patches**
  - **Elongated by Wind**
  - **Ribbons of Thicker Oil Surrounded by Thinner Oil**

Table 2 - 3 Oil viscosity ranges

Viscosity Ranges		
light	**medium**	**heavy**
		
free flowing (like water)	**slowly pouring (like molasses)**	**barely flowing (like tar)**
• diesel • gasoline • heating oil • kerosene	• Bunker A • Fuel Oil No.4 • lubricating oils • medium crudes	• Bunker B and C • Fuel Oil No.6 • weathered crudes • bitumen

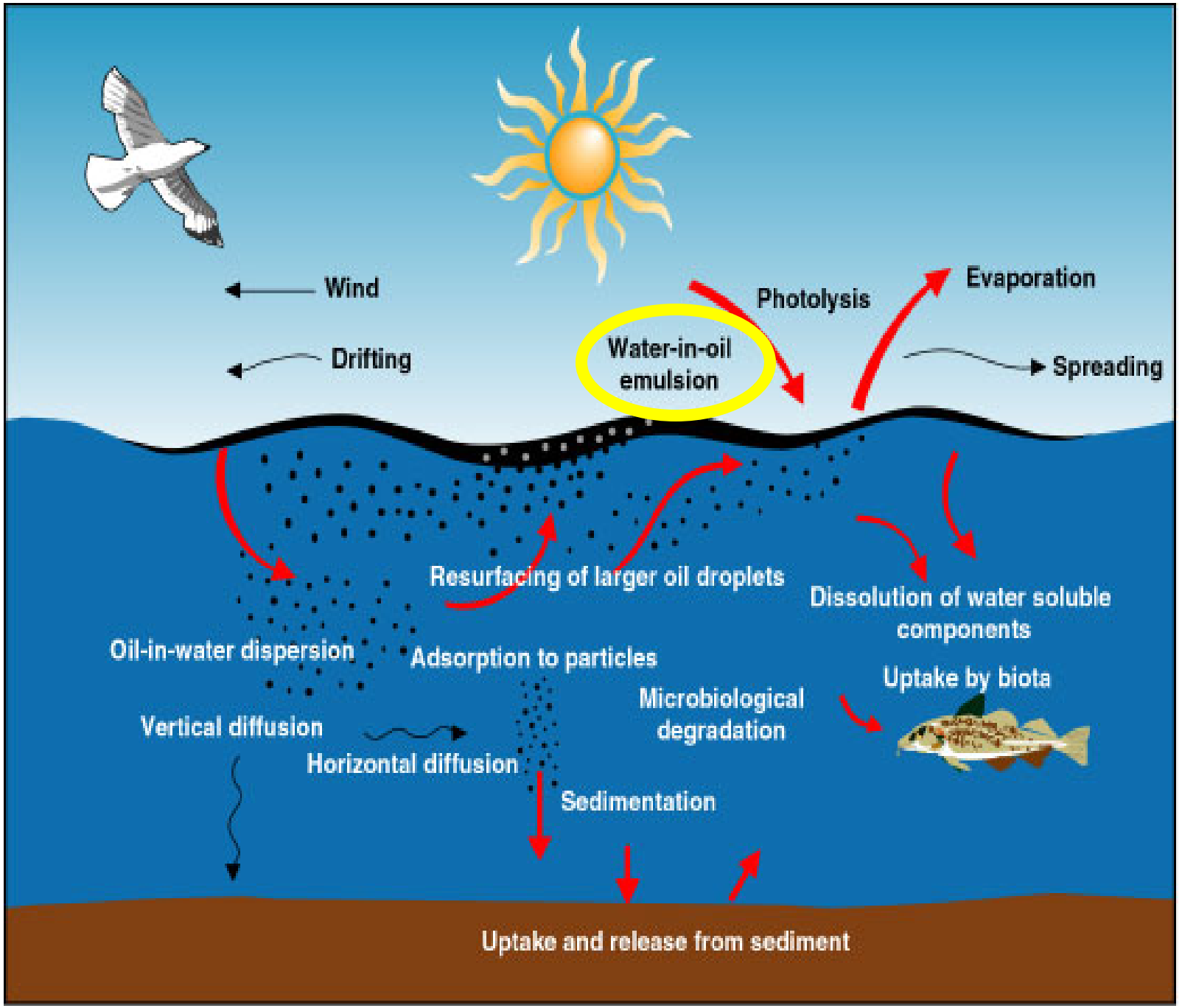
More Viscose Spreads, But It Takes Longer

Thickness of Oil (inches)



Time in hours

Medium Crude, First 48 Hours, Calm Seas, Low Wind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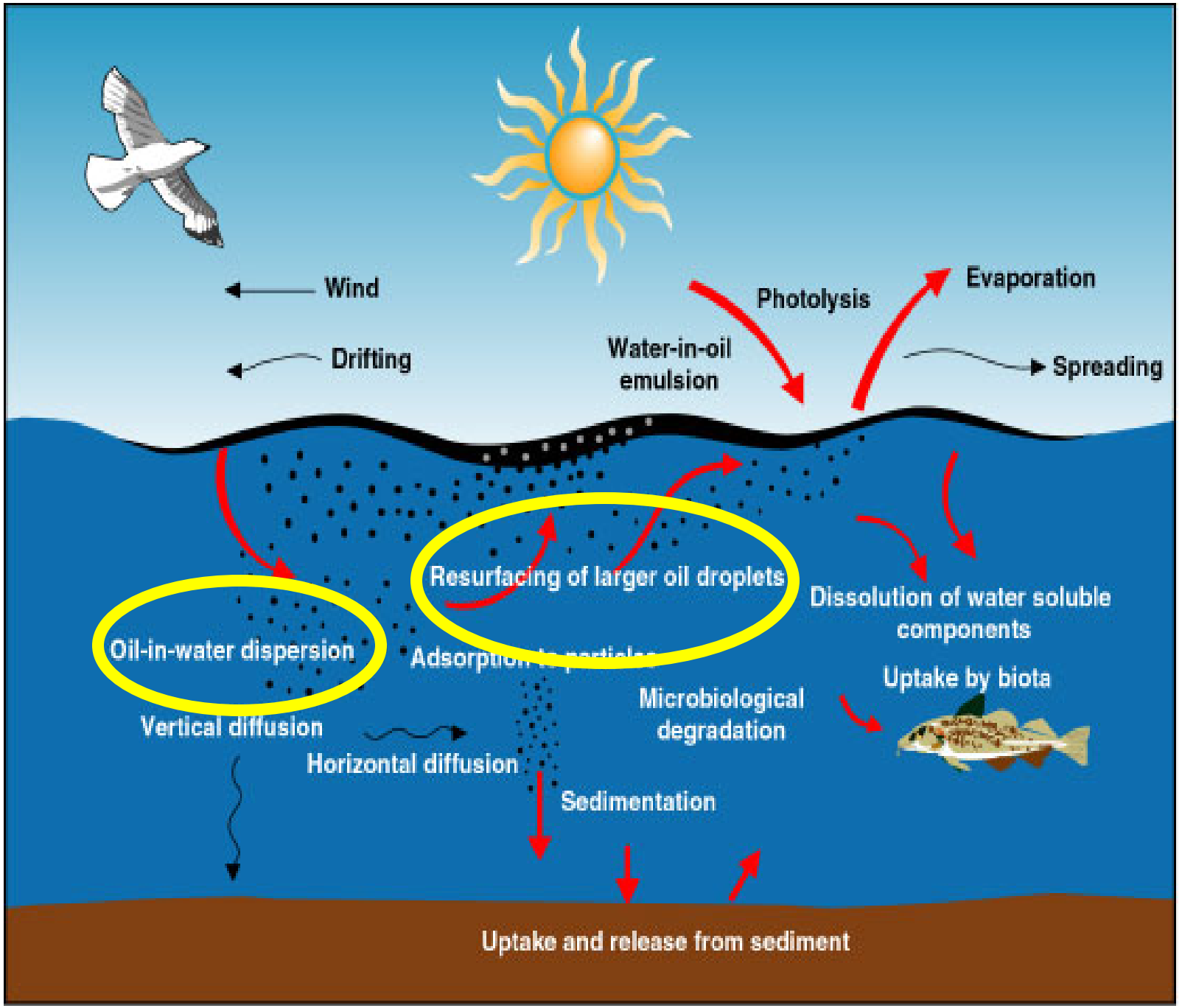
Other Things that Happen to Slick

- **Emulsification ("Chocolate Mousse")**
  - **Water Gets Into Oil (water in oil emulsions)**
    - **60 to 85% Water gets Mixed into Oil**
    - **Expands Oil Volume 3 to 5 Times**
    - **Hard to Get Water Out Once Mixed In (Very Stable)**
    - **Makes Oil Much More Viscose**
    - **Oil Sinks Lower in Water Column**
    - **Oil Evaporates Slower**
    - **Once Formed They Stay in Environment Long Time**
    - **More Common with Heavy Crudes**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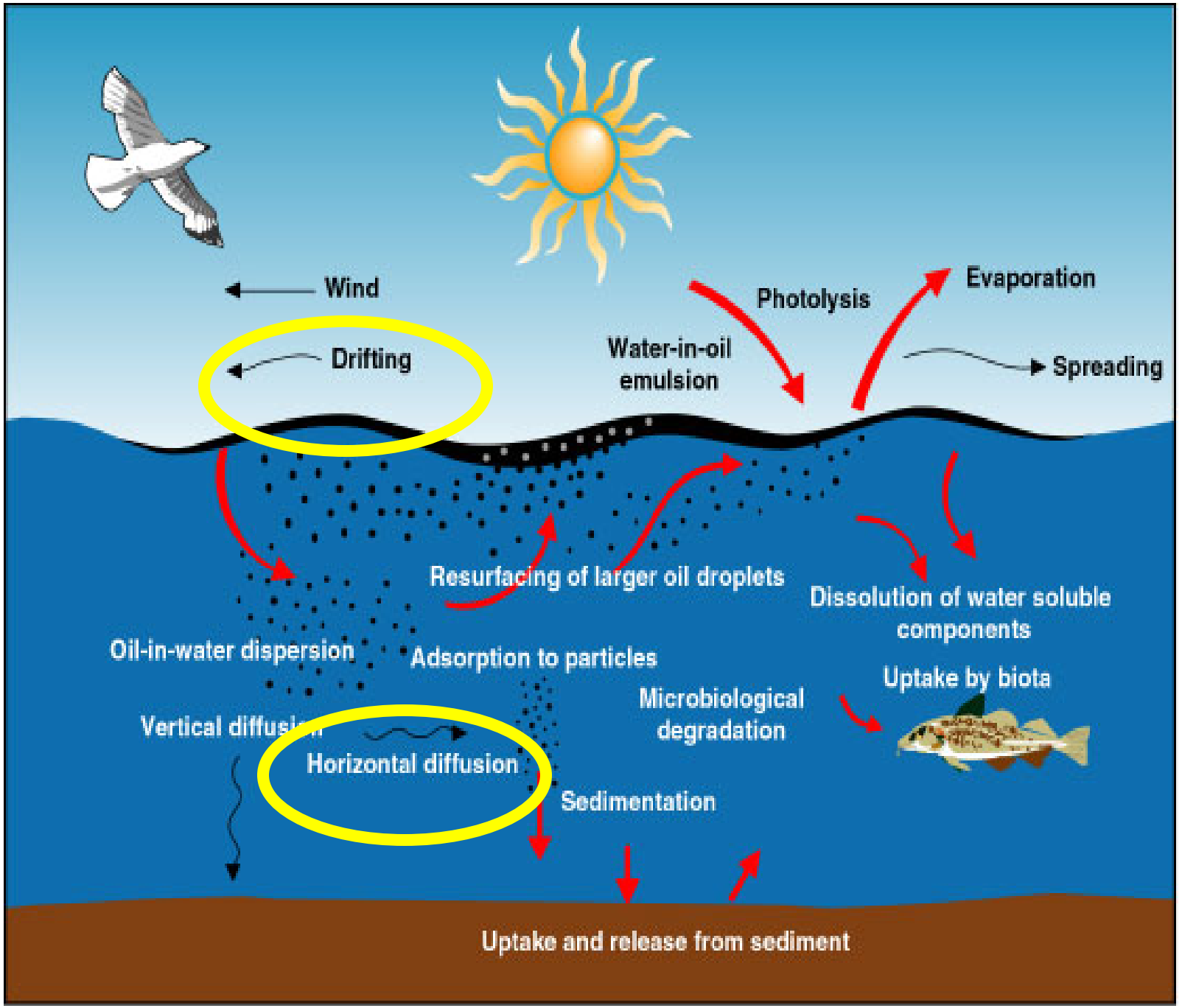
Other Things that Happen to Slick

- **Vertical Dispersion**
  - **Small Droplets of Oil Created by Turbulence**
    - **Wind and Waves Cause Droplets to Break Away from Slick**
    - **Some Droplets Re-Surface**
    - **Very Tiny Droplets Stay in Water Column**
- **Amount Dispersion Function of Wind Speed, Oil Viscosity, Slick Thickness and Other Factors**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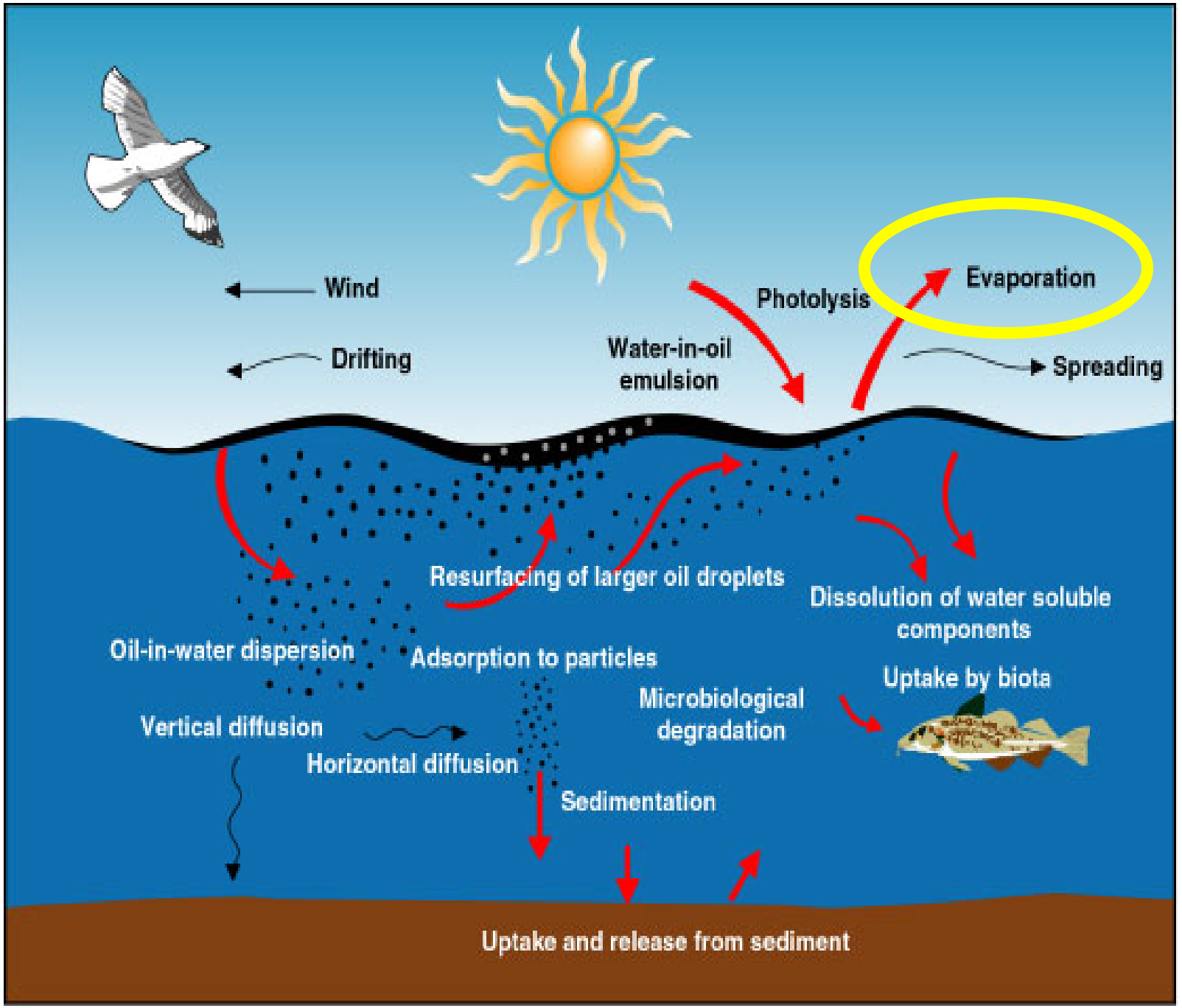
Other Things that Happen to Slick

- **Horizontal Dispersion**
  - **Movement of Oil Away from Point of Spill**
    - **Of Slick (Drifting)**
    - **Of Oil in Water**
  - **Largely Function of Wind, Waves and Currents**
  - **Horizontal Dispersion Occurs for Long Time**
    - **Spreading Occurs for about 1 Day**

Other Processes that Happen to Oil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Evaporation

Pathway	Estimated Time Scale (days)	Percent Initial Oil
Evaporation (volatility)	**1-10**	**25**

- **Oil Characteristic: Volatility (boiling point)**
- **Function of Wind Speed, Area of Slick, Temperature Air and Water, and Other Factors**

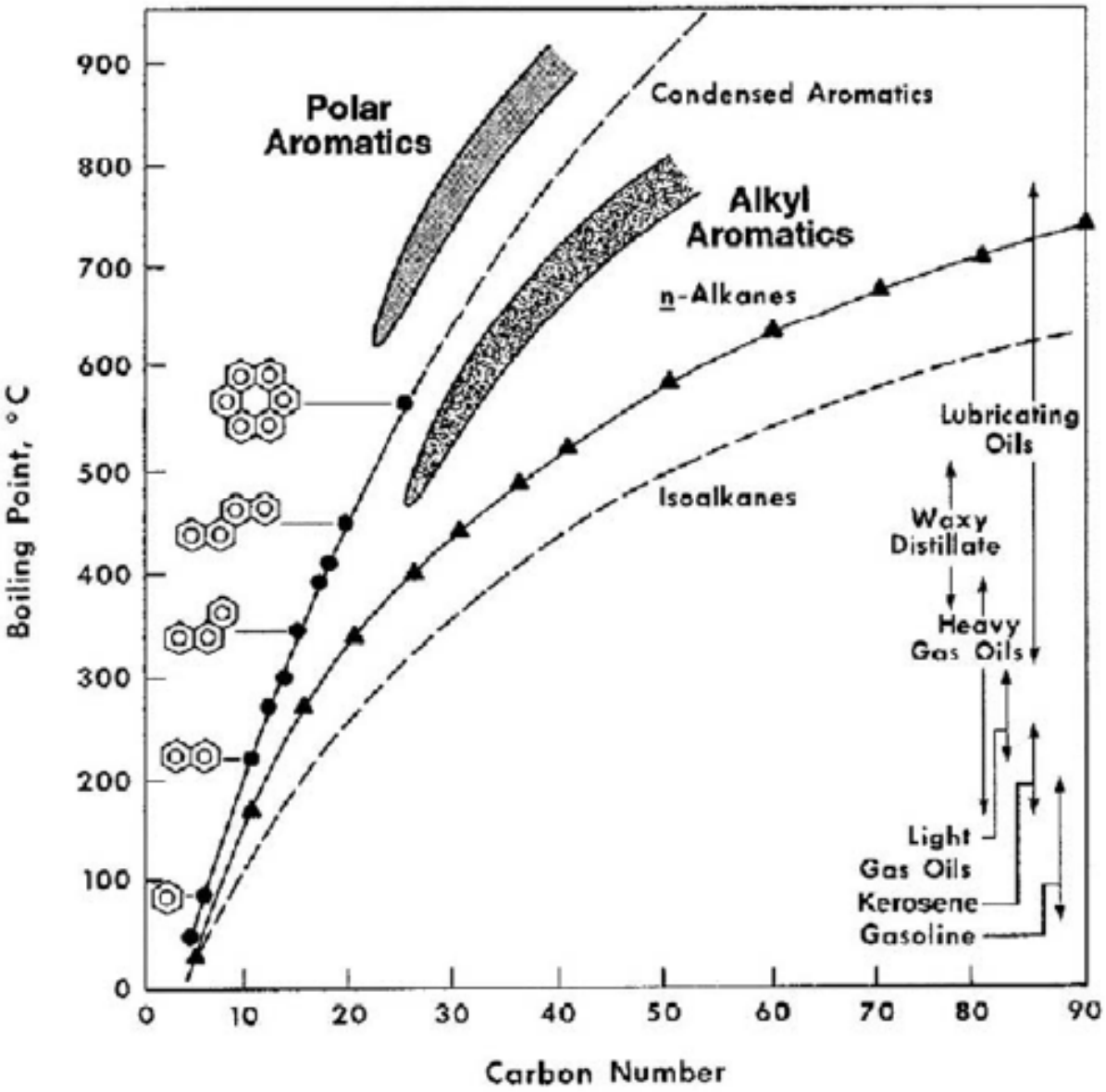


Figure 8-13 The relationship of boiling point to carbon number for aromatics, *n*-alkanes, and isoalkanes.

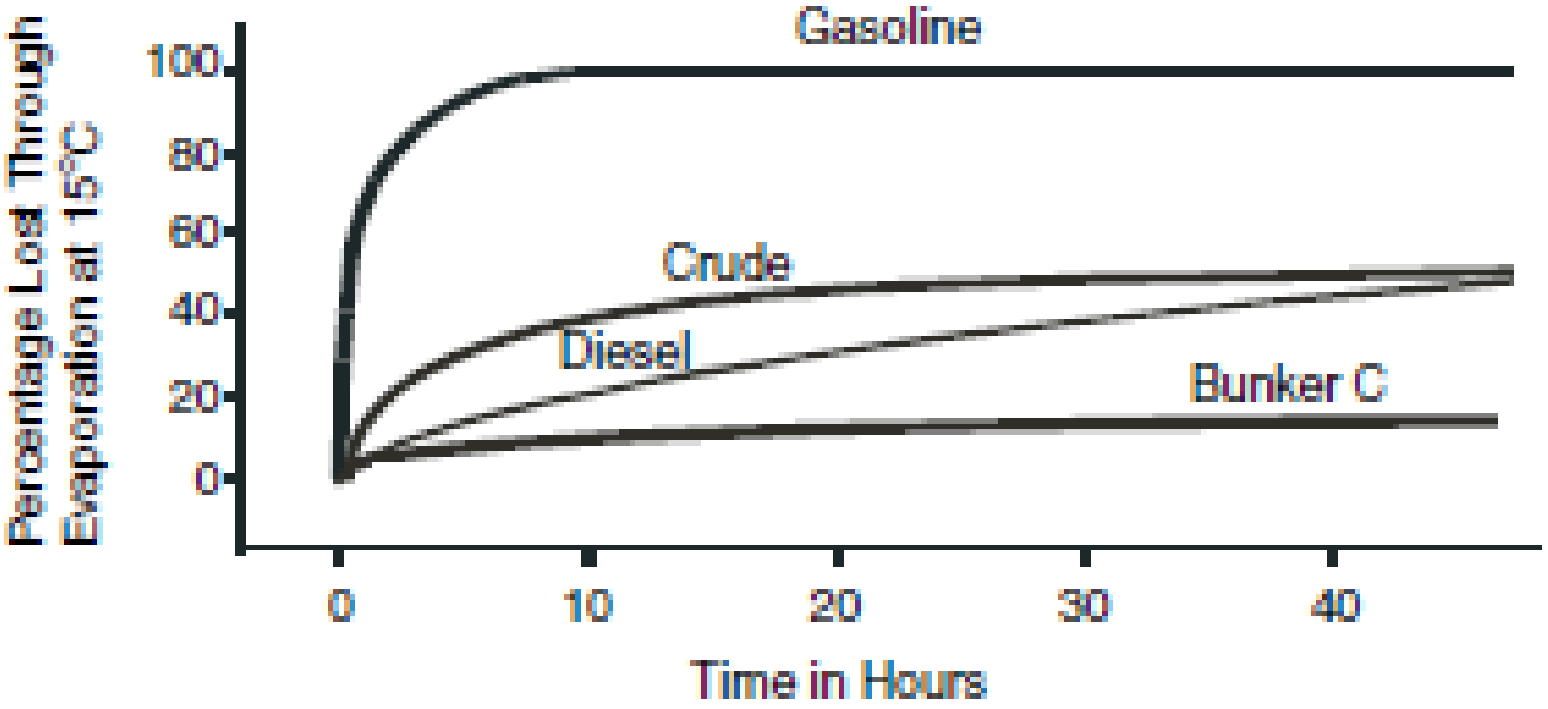
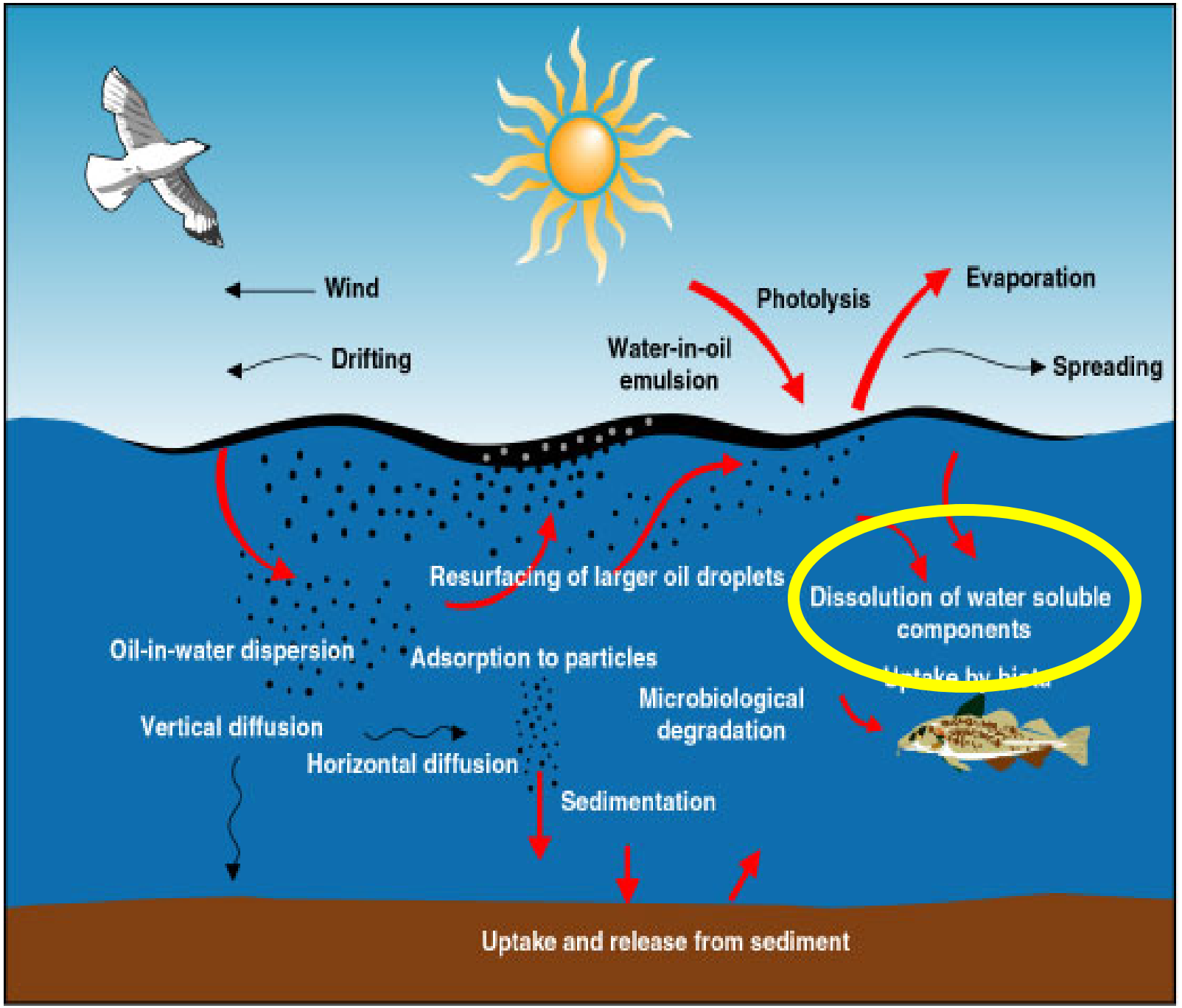


FIGURE 4-2 Evaporation rates of different types of oil at 15°C **(~60°F)** (adapted from Fingas, 2000).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Dissolution into Water

Pathway	Estimated Time Scale (days)	Percent Initial Oil
Dissolution (solubility)	1-10	5

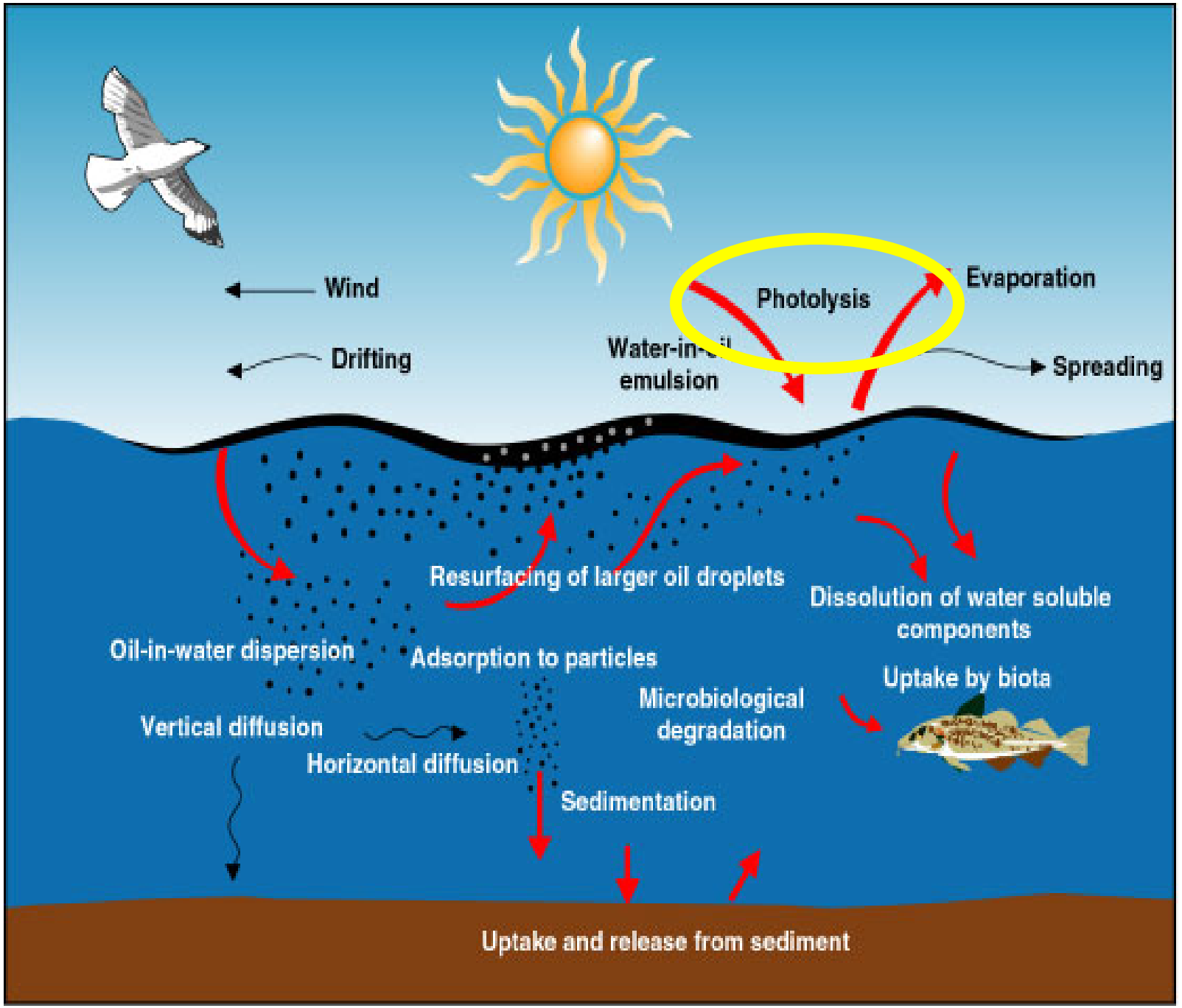
- Oil Characteristic: Solubility of Compounds in Water
- Function of Temperature and Salinity of Water
- Type of Crude Oil Compound

TABLE 4-3 Examples of Whole Oil Solubility Data

Oil Type	Solubility mg/L	Temperature °C	Salinity %
Prudhoe Bay	29	22	distilled
Lago Media	24	22	distilled
Lago Media	16.5	22	33
Diesel fuel	3	20	distilled
Diesel fuel	2.5	25	33
Bunker C	6	22	distilled
Automotive gasoline	98	22	distilled

Table 4.17 Solubilities of various hydrocarbons and crude oil fractions in water

Hydrocarbon or crude oil fraction	Carbon No.	Solubility in water, mg/L
Normal paraffins	C_5	40
	C_6	10
	C_7	3
	C_8	1
	C_{12}	0.01
	C_{30}	0.002
Aromatics	C_6 (benzene)	1,800
	C_7 (toluene)	500
	C_8 (xylenes)	175
	C_9 (alkylbenzenes)	50
	C_{14} (anthracene)	0.075
	C_{18} (chrysene)	0.002
Kerosene	C_{10}–C_{17}	0.2–0.0001
Gas oil	C_{16}–C_{25}	3×10^{-4}–1×10^{-8}
Lube oil	C_{23}–C_{37}	1×10^{-7}–1×10^{-14}
Bitumen, etc.	$>C_{37}$	$<1 \times 10^{-14}$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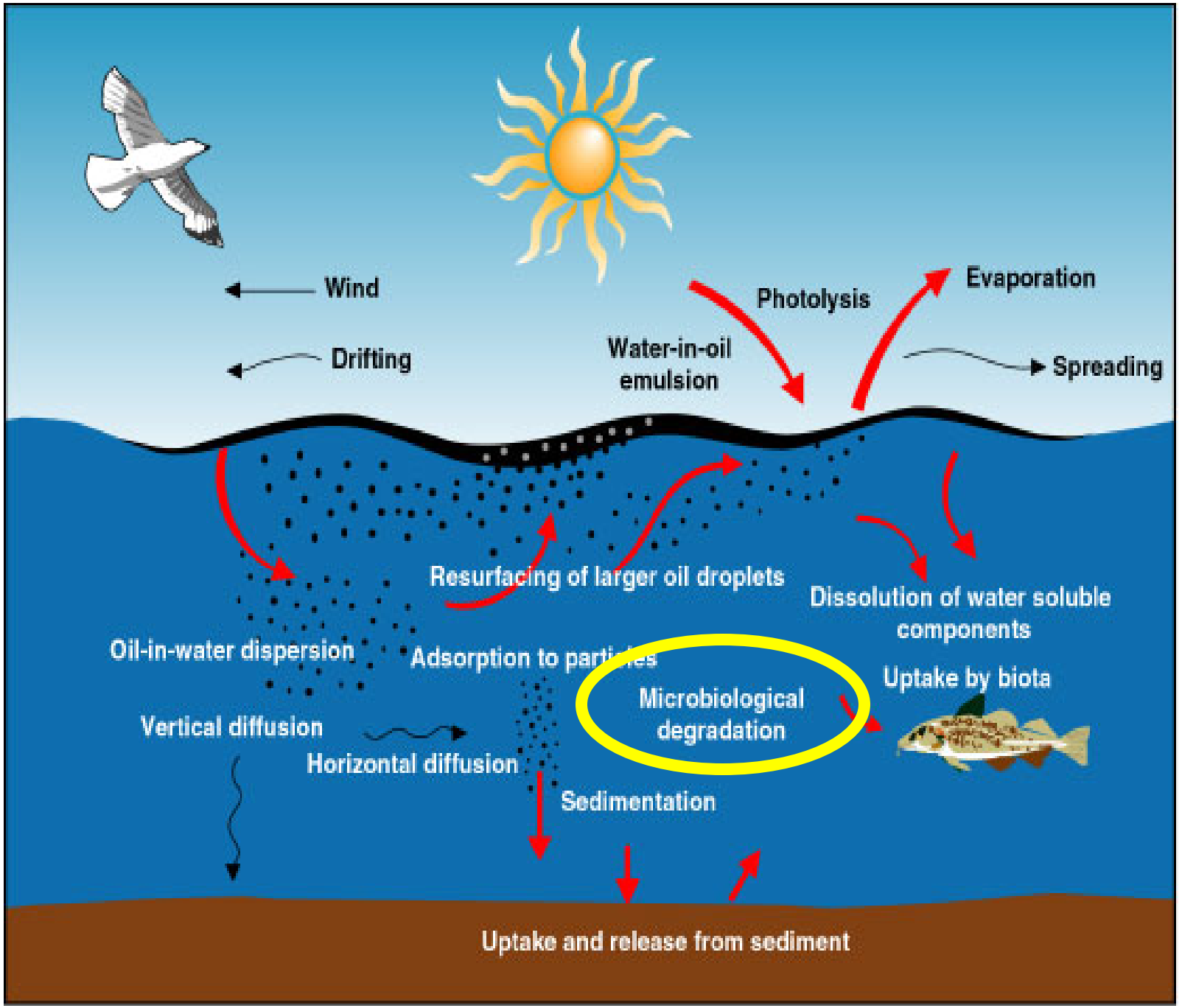
Photochemical Degradation

Pathway	Estimated Time Scale (days)	Percent Initial Oil
Photochemical Breakup (Sun)	10-100	5

- Light Energy from Sun and Oxygen from Air Breakdown Oil Compounds into Smaller Molecules
- Complex Process, But Can Create Products that Are More soluble in Water and Sometimes More Toxic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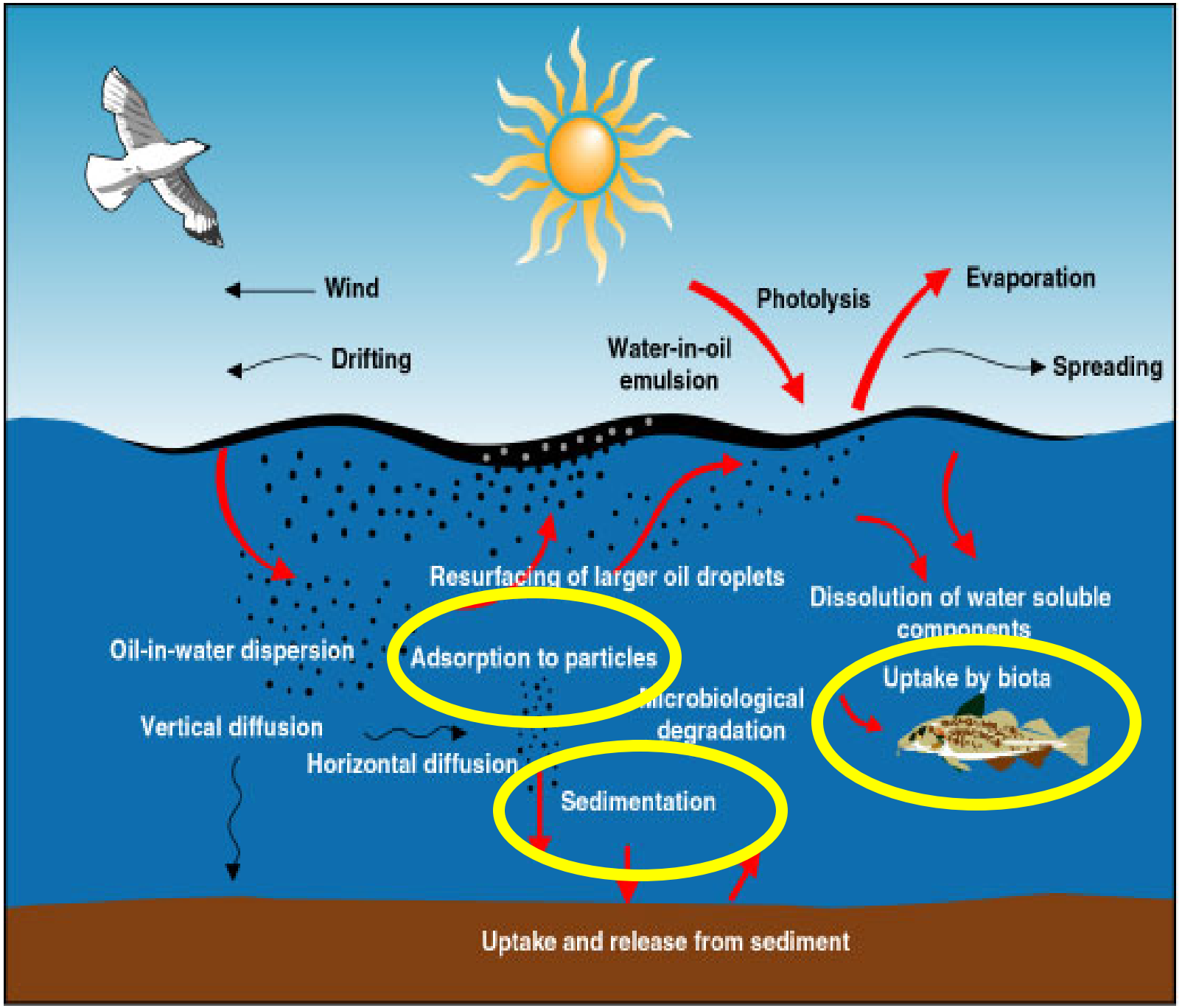
Biodegradation

Pathway	Estimated Time Scale (days)	Percent Initial Oil
Biodegradation	50 -500	30

- Microorganisms Degrade Oil Compounds (Use to Make Energy)
  - Not All Microbes
  - Temperature Impacts
  - Usually Best If Oxygen Available to Microbes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What Happens to Remaining Oil

Pathway	Estimated Time Scale (days)	Percent Initial Oil
Disintegration and Sinking	100-1000	15
Residue	More Than 100	20

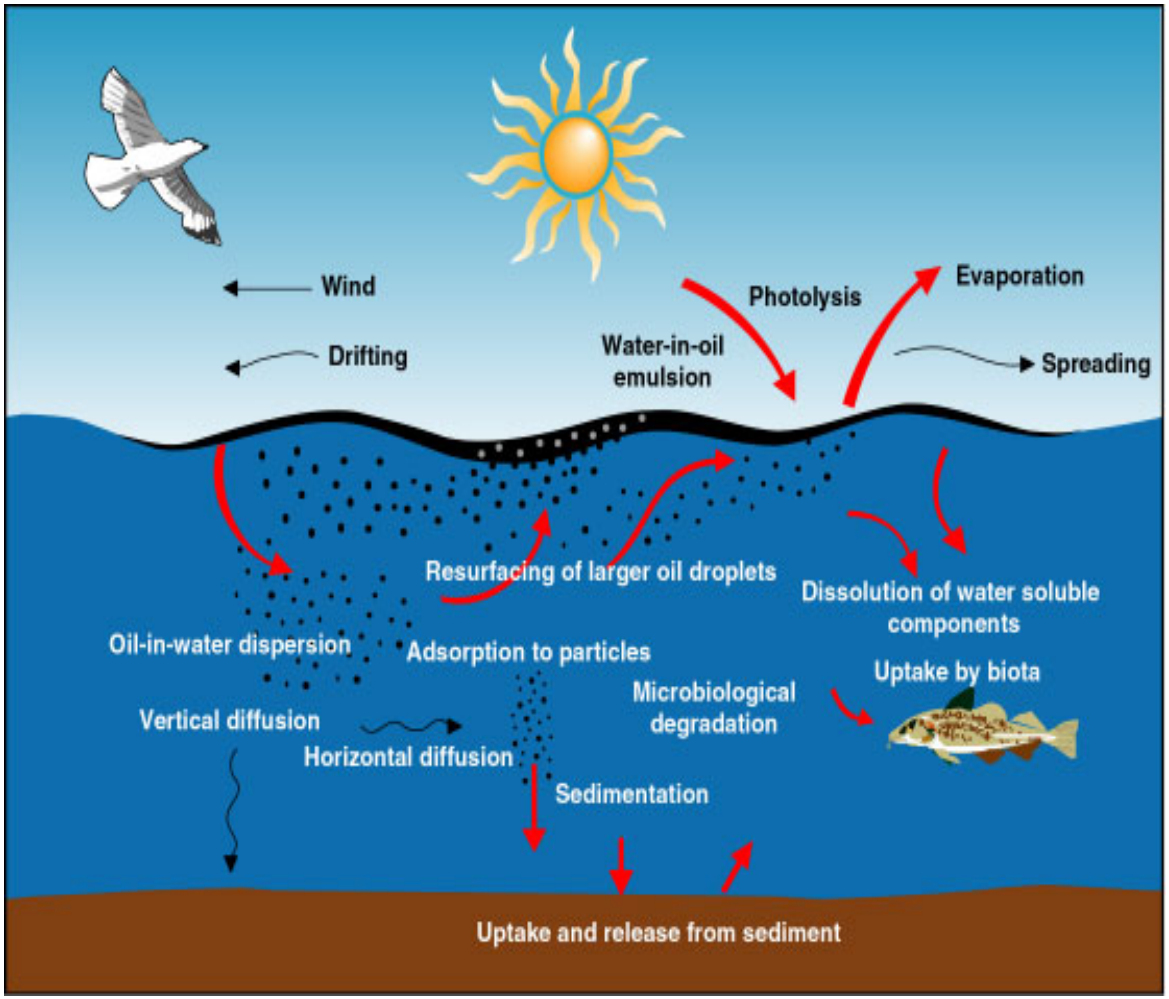
What Happens to Remaining Oil

- Sticks to Particles in Water (Adsorption) and Sinks (Sedimentation)
  - Often Goes into Sediments on Bottom
- Forms Tarballs (Asphaltic Compounds) Lots of Carbons (up to 150), Very Resistant to Degradation
- Uptake by Organisms
  - Research Being Conducted Now

Summary

Natural Processes for Surface Oil Slicks

- Function of:
- Oil Type and Characteristics
- Environmental Conditions
  - Temperature
    - Water, Air
  - Wind
  - Waves
  - Currents, Tides



Pathway (Butler et al., 1976)	Estimated Time Scale (days)	Percent Initial Oil
Evaporation (volatility)	1-10	25
Dissolution (solubility)	1-10	5
Photochemical Breakup (Sun)	10-100	5
Biodegradation	50 -500	30
Disintegration and Sinking	100-1000	15
Residue	More than 100	20
Total		100

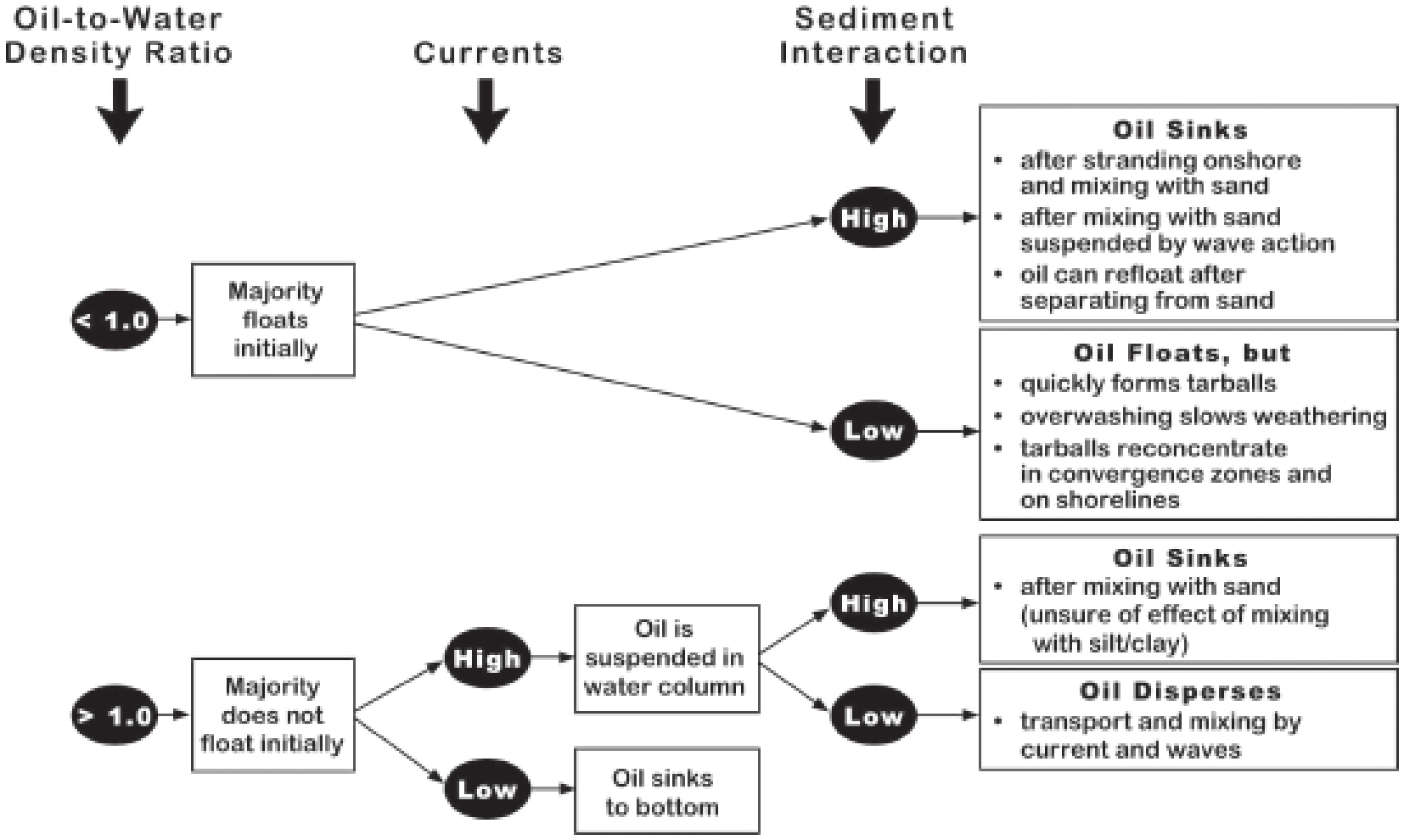


FIGURE 4-5 Factors determining whether spilled oil will float or sink (NRC, 1999).

TABLE 4-7 Processes that Move Petroleum Hydrocarbons Away from Point of Origin

	Weathering									
Input Type	Petroleum Persistence	Evaporation	Emulsification	Dissolution	Oxidation	Horizontal Transport or Movement	Vertical Transport or Movement	Sedimentation	Shoreline Stranding	Tarballs
Seeps	years	H	M	M	M	H	M	M	H	H
Spills										
Gasoline	days	H	NR	M	L	L	L	NR	NR	NR
Light distillates	days	M	L / L	H	L	M	H	L	L	NR
Crudes	months	M	M	M	M	M	M	M	H	M
Heavy distillates	years	L	M	L	L	H	L	H	H	H
Produced water	days	M	NR	M	M	L	L	L	L	NR
Vessel operational	months	M	L	M	L	M	L	L	L	M
2-stroke engines (gasoline & light distillates)	days	H	NR	M	L	L	L	L/NR	NR	NR
Atmospheric	days	H	NR	M	M	H	NR / NR	L	NR	NR
Land based	U	M	L	L	L	M	M	M	NR	U

NOTE: H = high; L = low; M = moderate; NR = not relevant; U = unknown

Oxidation = Photochemical Degradation and Biodegradation

Thank You So Much for Participating in These Talks

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