Introduction to Dispersants

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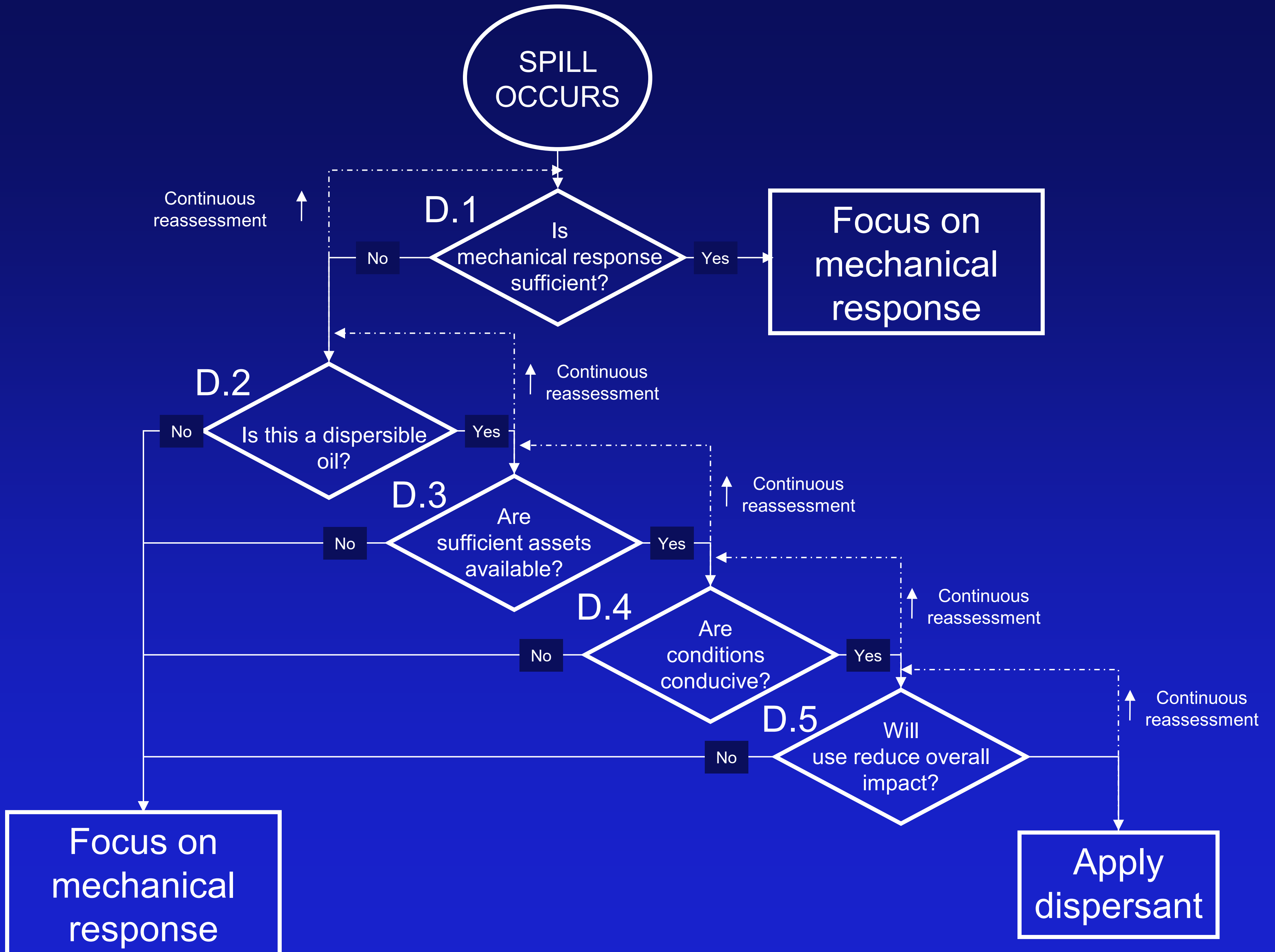
Bradford Benggio, NOAA SSC


SPILL OCCURS
Continuous reassessment
D.1
Is mechanical response sufficient?
No
Yes
Focus on mechanical response
D.2
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Continuous reassessment
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D.5
Will use reduce overall impact?
No
Continuous reassessment
Focus on mechanical response
Apply dispersant

What are They?

How Do They Work?

What Factors Affect Dispersant Effectiveness?

What is the Window of Opportunity for Effective Use of Dispersants?

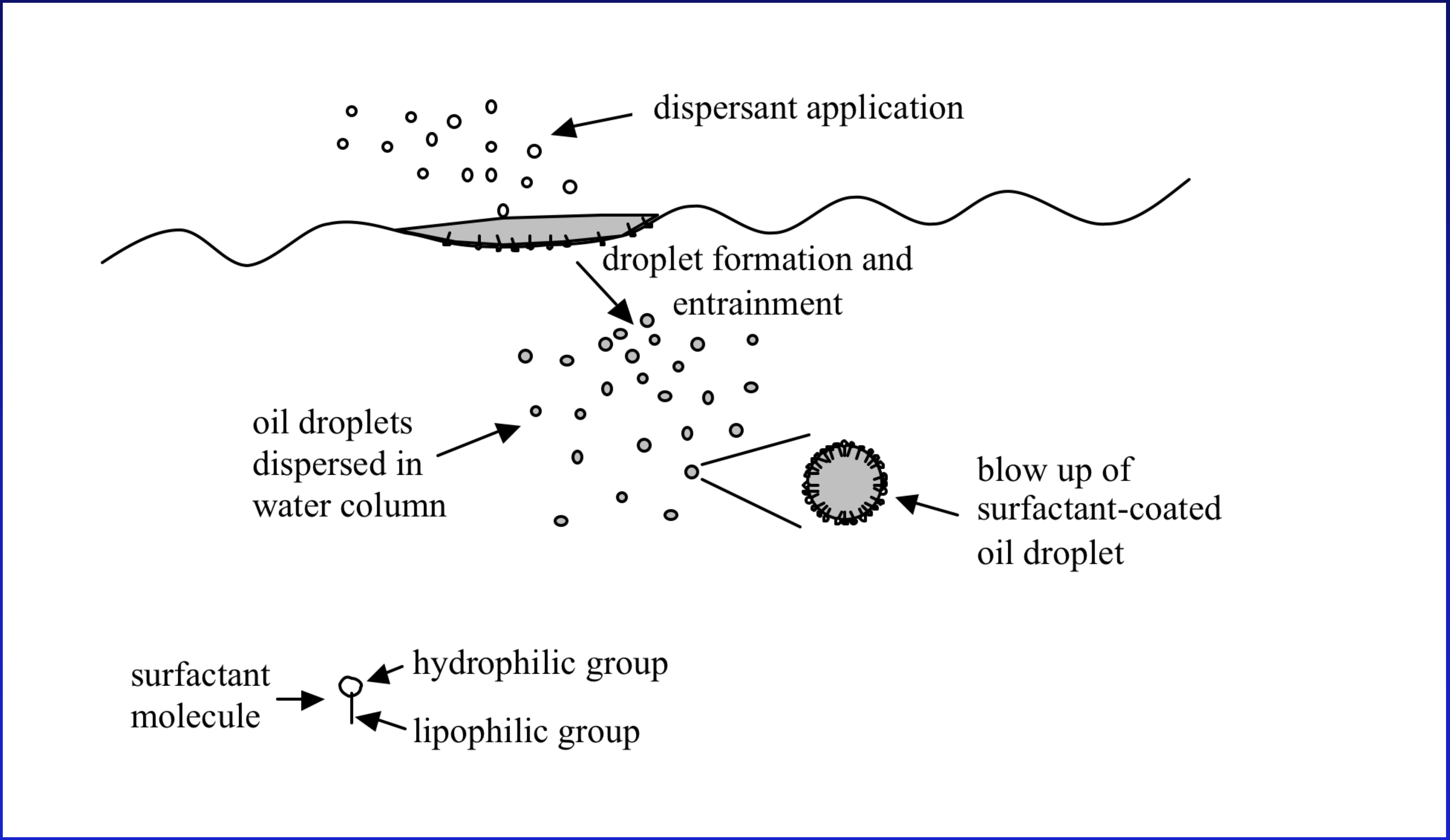
What are Dispersants?

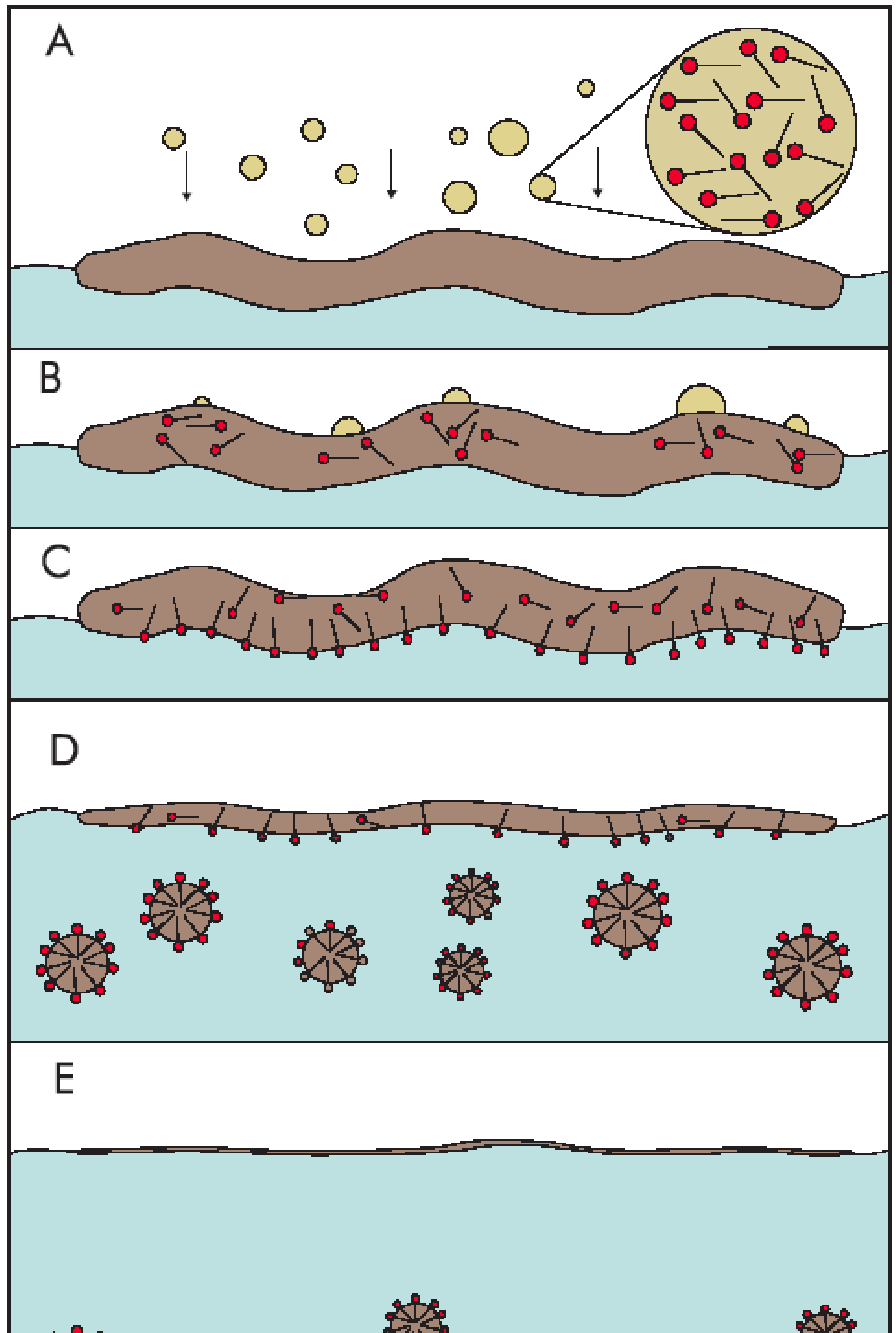
- Mixture of three types of chemicals:
  - Solvents
    - Promote dissolution into a homogeneous mixture
    - Reduce viscosity
    - Increase solubility in oil
  - Additives
    - Improve dissolution into the oil
    - Increase stability of the formulation
  - Surface-active Agents (Surfactants)

What are Surfactants?

- Compounds containing both oil-compatible and water-compatible groups
- Aka "soap"
- Surfactant molecules orient at the oil-water interface
- Objective is to reduce the oil-water interfacial tension, allowing the formation of a larger number of smaller oil droplets

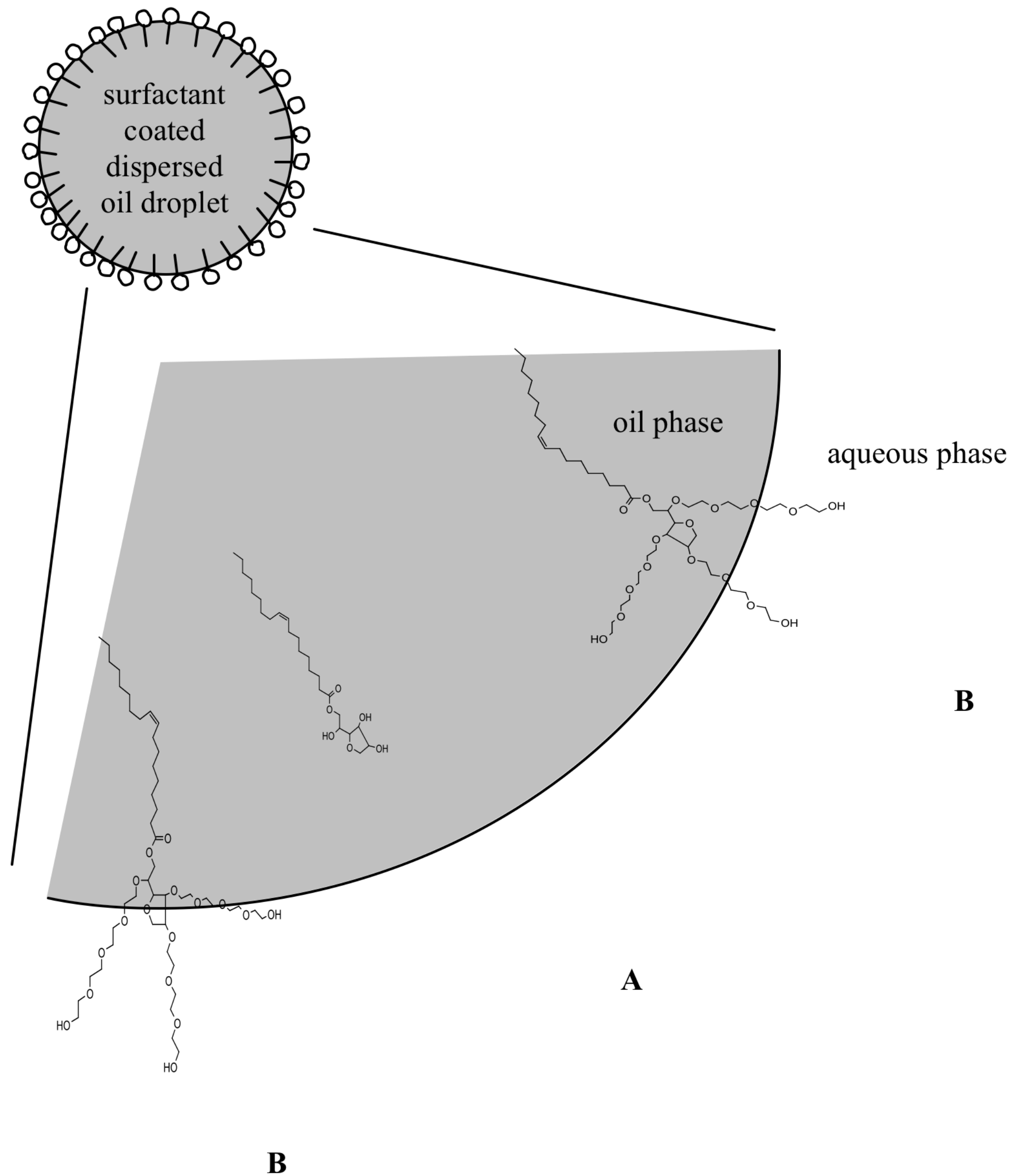
Mechanism of Chemical Dispersion




A
B
C
D
E

Orientation of two surfactants at the oil:water interface in a dispersed oil droplet

Use of 2+ surfactants of different properties increases packing



Composition of Corexit Dispersants

- Both contain a mixture of nonionic (48%) and anionic (35%) surfactants:
  - Ethoxylated sorbitan mono- and trioleates
  - Sorbitan monooleate
  - Sodium dioctyl sulfosuccinate

Composition of Corexit Dispersants

- Corexit 9527 solvent
  - Glycol ether (2-butoxyethanol)

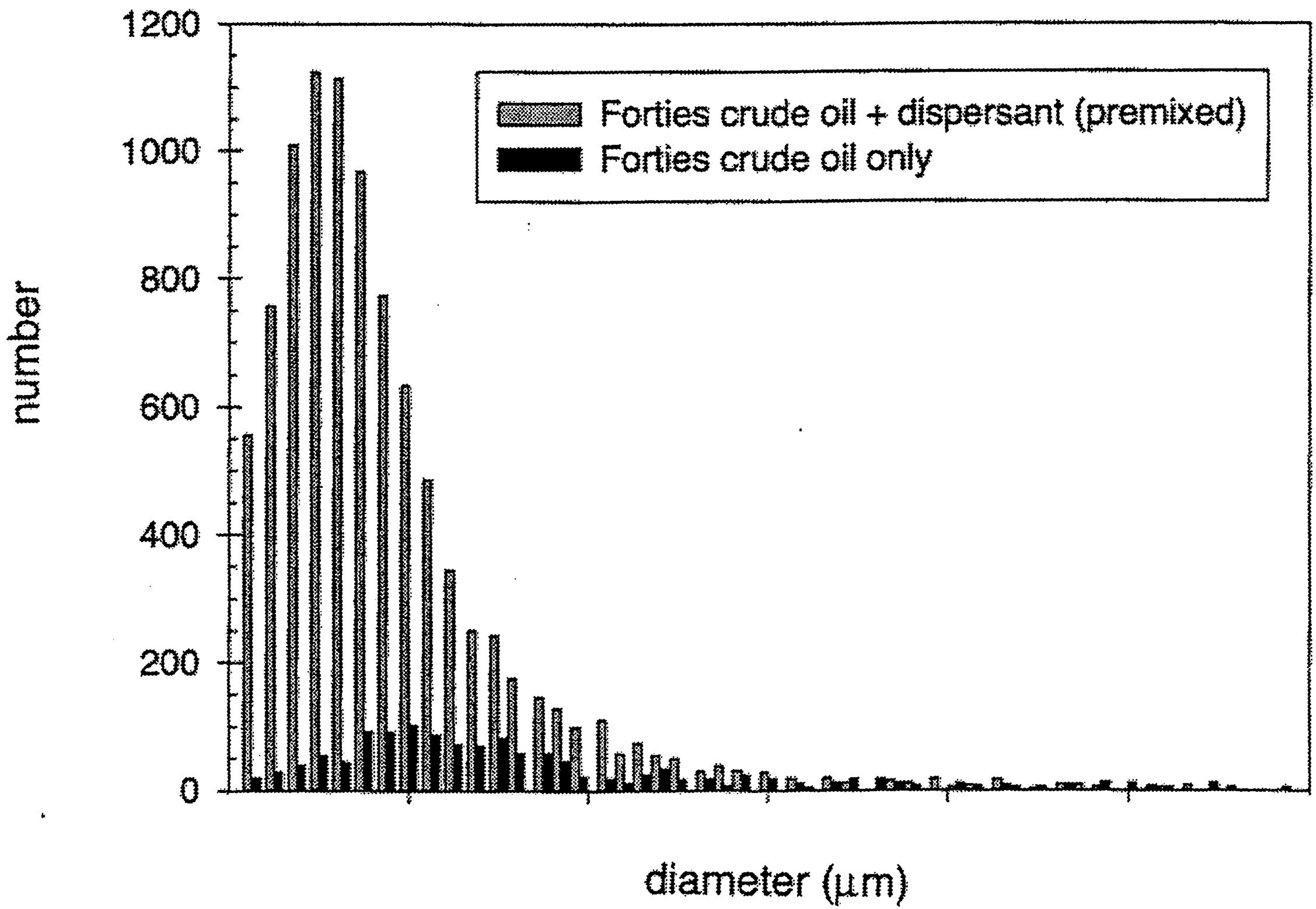
- Corexit 9500 solvent
  - Food-grade aliphatic hydrocarbons (Norpar 13; n-alkanes ranging from nonane to hexadecane)

Reasons for Change in 9500

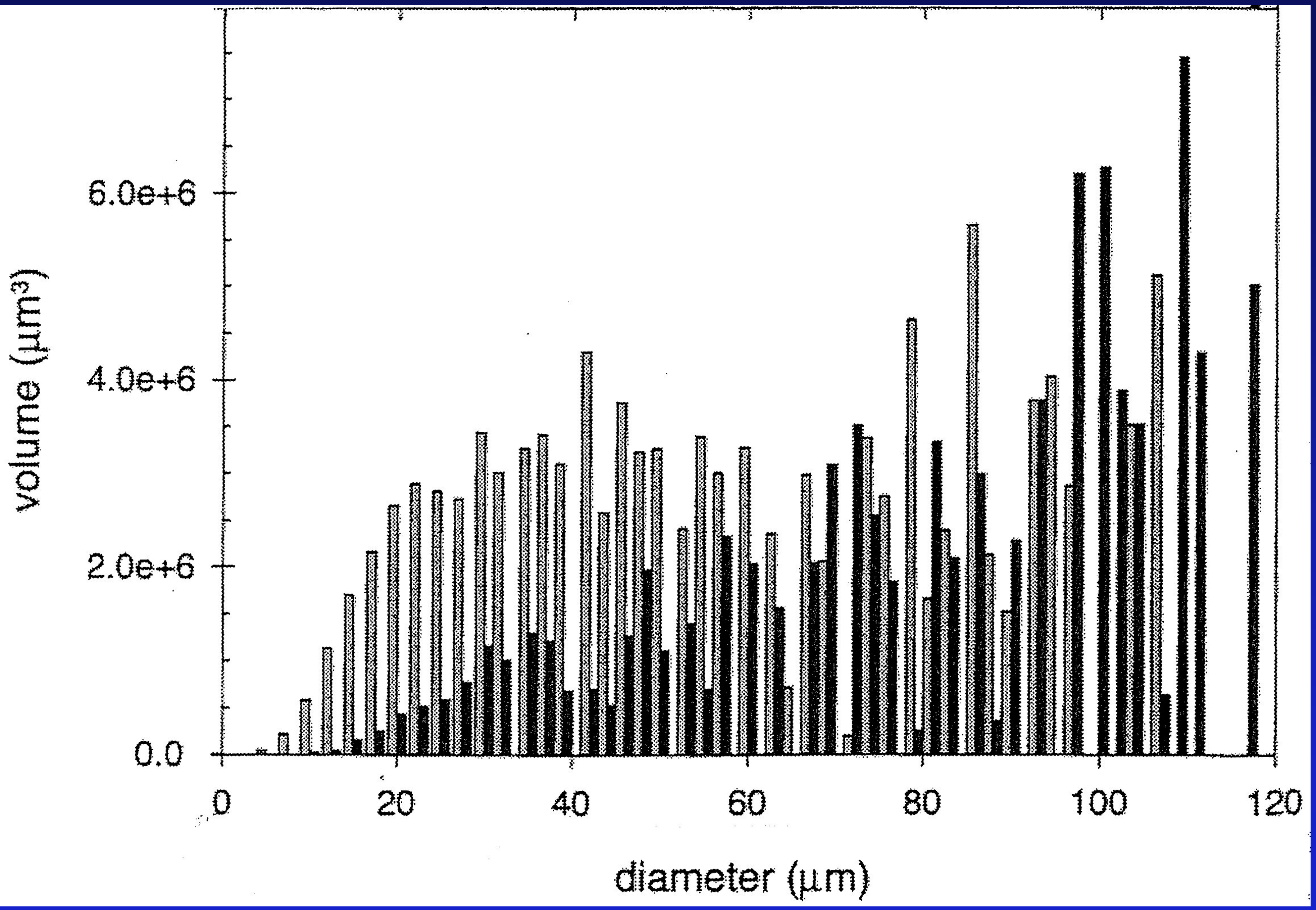
- Prolonged exposure to Corexit 9527 caused adverse health effects in some responders due to the glycol ether solvent
- New solvent more effective on high-viscosity oils

How Do Dispersants Work?

- Reduce the oil-water interfacial tension
- Allows turbulent shear to govern droplet formation
- Leads to larger numbers of smaller droplets (~ 10 microns)
- Smaller droplets less likely to resurface



1200
1000
800
600
400
200
0
number
Forties crude oil + dispersant (premixed)
Forties crude oil only
diameter (µm)



volume (μm³)
6.0e+6
4.0e+6
2.0e+6
0.0
0
20
40
60
80
100
120
diameter (μm)

Requirements for Effective Dispersant Application (NRC 1989)

1. The dispersant must hit the target oil at the desired dosage.
2. The surfactant molecules in the dispersant must have time and energy to penetrate and mix into the oil.
3. The surfactant molecules must orient at the oil-water interface with the hydrophilic groups in the water phase and the lipophilic groups in the oil phase.

Requirements for Effective Dispersant Application (NRC 1989)

4. The oil-water interfacial tension must decrease due to the presence of the surfactant molecules at the oil-water interface, thereby weakening the cohesive strength of the oil film.
5. Sufficient mixing energy must be applied at the oil-water interface (by wind and/or wave action) to allow generation of smaller oil droplets (with a concomitant increase in interfacial surface area).

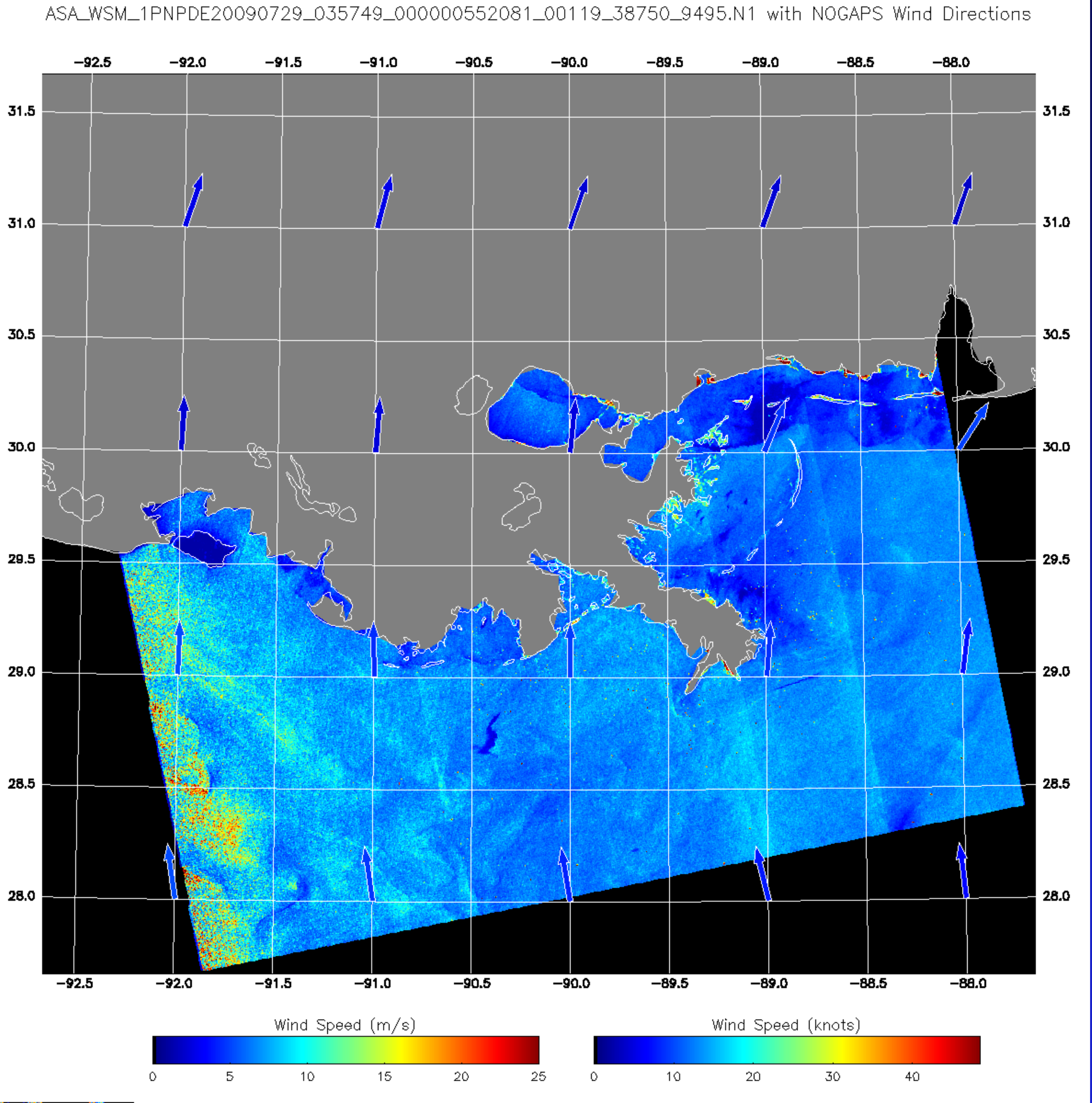
Requirements for Effective Dispersant Application (NRC 1989)

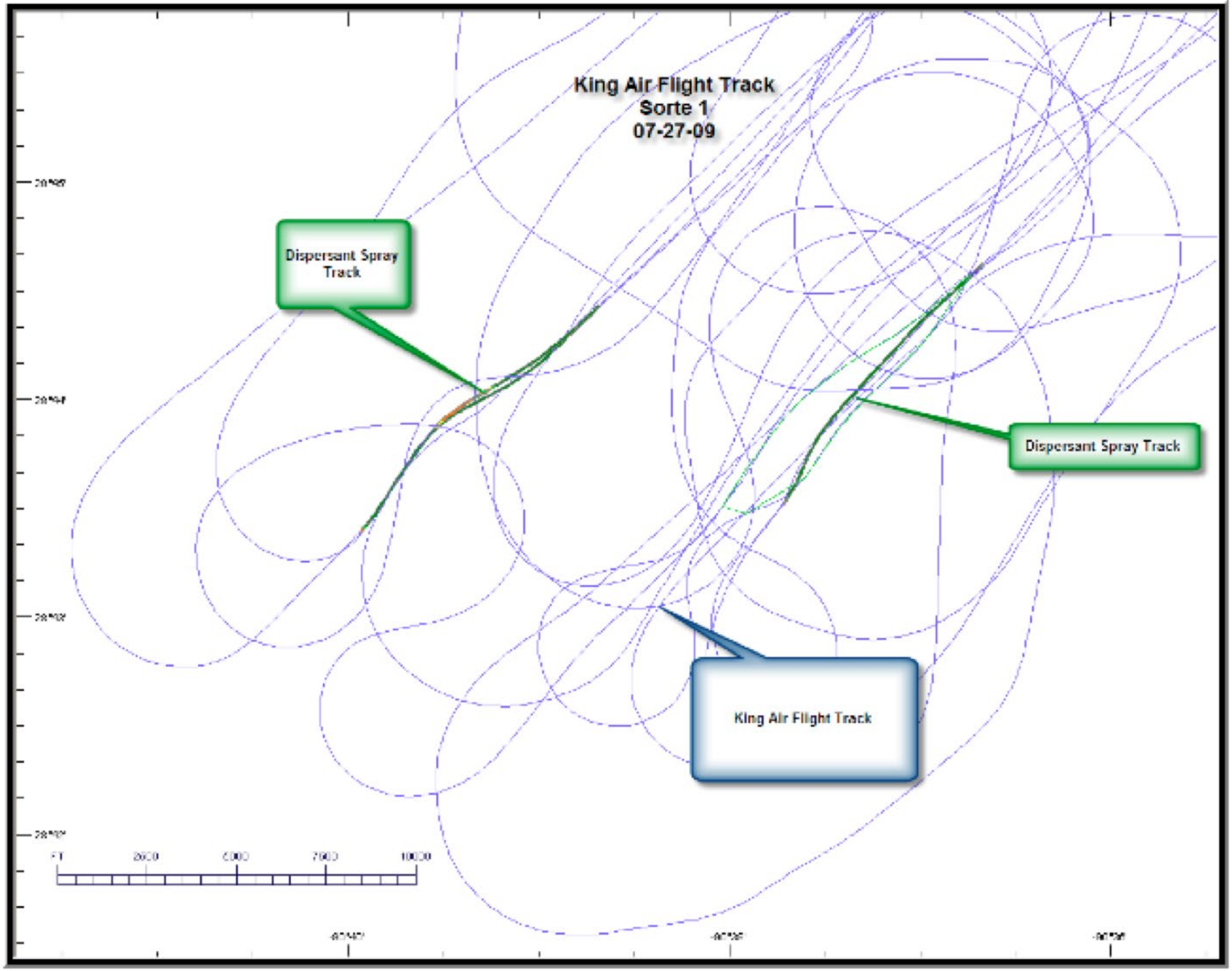
6. The droplets must be dispersed throughout the water column by a combination of diffusive and advective processes to minimize droplet-droplet collisions and coalescence to form larger droplets (which can resurface in the absence of continued turbulence).
7. After entrainment, the droplets must be diluted to nontoxic concentrations and remain suspended in the water column long enough for the majority of the oil to be biodegraded.

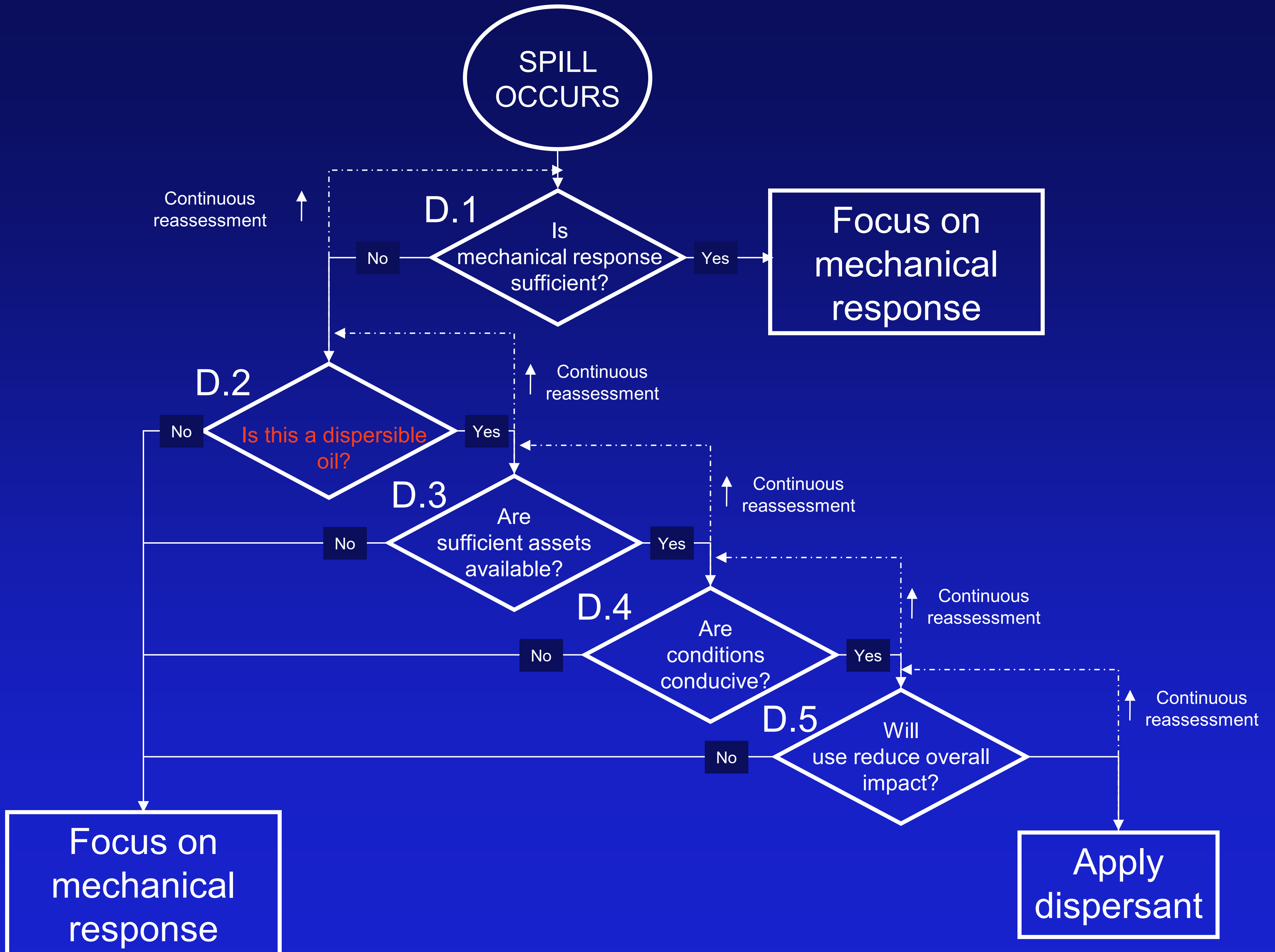
GOM Pipeline Spill 07/09

63,000 gal
S La Crude

SAR Image




King Air Flight Track
Sorte 1
07-27-09
Dispersant Spray Track
Dispersant Spray Track
King Air Flight Track
FT
10000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Is the Oil Dispersible?

- Is the fresh oil dispersible?
  - Evaluate oil properties
  - Review lab effectiveness results
- If yes, how long before it becomes non-dispersible?
  - Predict changes in properties for spill conditions (models, field observations)

Lab vs Field Dispersant Effectiveness

Oil	Dispersant	Field	Lab
MFO	9527	26%	42-91%
MFO	Slikgone	17%	23-94%
MFO	LA 1834	4%	2-50%
Forties	Slikgone	16%	25-95%
Forties	LA 1834	5%	12-61%
Ratio L/F	0.19-0.62		

Lab vs Field Dispersant Effectiveness

Lab Test	Ratio Lab:Field
Swirling Flask	0.4
French IFP	0.2
Warren Springs 1	0.56
Warren Springs 2	0.62
Exdet	0.27

What is the Window of Opportunity for Effective Use of Dispersants?

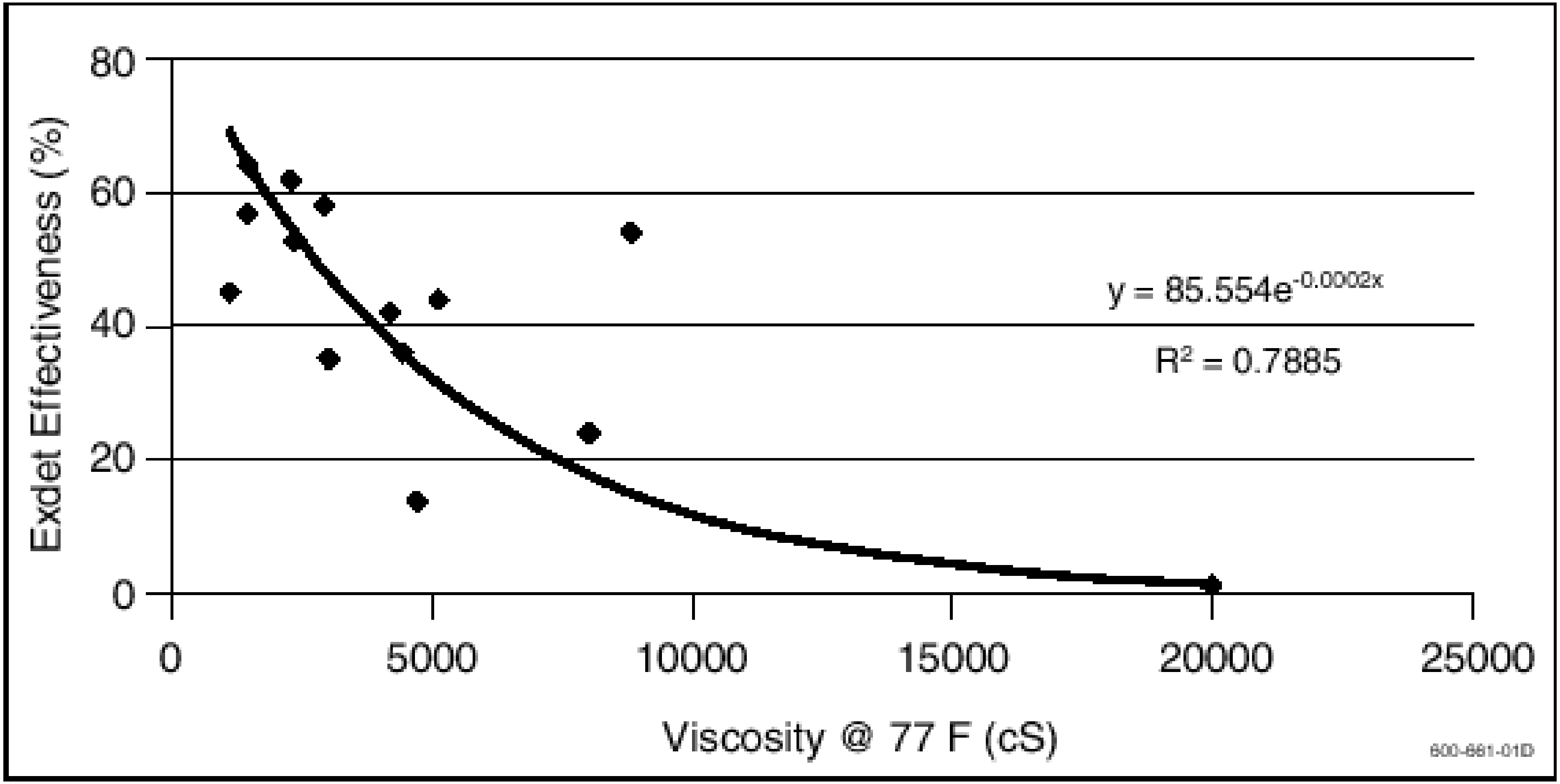
- Most important weathering processes are:
  - Evaporation
  - Formation of stable water-in-oil emulsions
- Because they both affect the oil's viscosity on the water surface
- Both are affected by temperature and wind speed

Oil Properties Affecting Dispersant Effectiveness

- Viscosity
- Pour point
- Paraffin content
- Asphaltenes and resins content
- Tendency to form stable emulsions

These are all inter-related and affect viscosity, the key property

Effectiveness of Corexit 9500 vs Viscosity: swirling flask test, oil:dispersant ratio 20:1



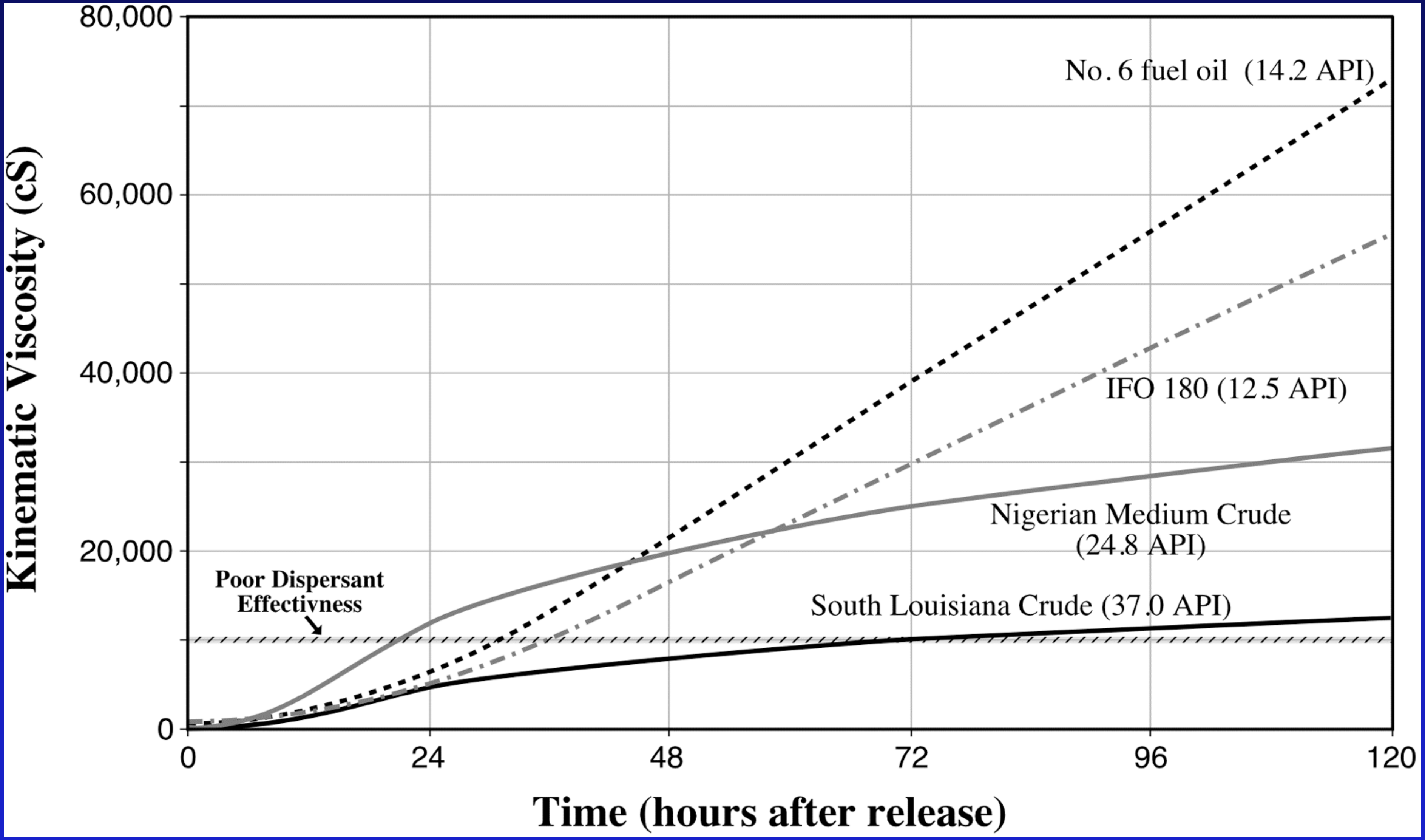
Viscosity of Liquids (20° C)

Liquid	Viscosity (cP)
Water	1
Kerosene	10
Olive oil	100
Glycerin or castor oil	1,000
Honey	10,000
Molasses	100,000
Peanut butter	250,000

Viscosity of Oils (14° C)

Oil	Viscosity (cP)
Fresh ANS crude	68
48-hr wx ANS	1,080
72-hr wx ANS	2,350
144-hr wx ANS	5,400

Predicted Viscosity 50,000 gal; 10 kt Wind; 75° F



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Oil Properties: Pour Point

- Temperature above which an oil will flow.
- If ambient temperature is above pour point the oil will behave as a liquid.
- If ambient temperature is below pour point the oil will behave as a semi-solid.

Oil Properties: Pour Point

Merey	-10° F
Mesa	-15° F
S. Louisiana	15° F
Nigerian Light	15° F
Prudhoe Bay	32° F
Nigerian Medium	45° F


LOSCO RESPONSE
12/3/2000 09:58

Oil Properties Affecting Dispersant Effectiveness

- Viscosity
- Pour point
- Paraffin content
- Asphaltenes and resins content
- Tendency to form stable emulsions

These are all inter-related and affect viscosity, the key property

Water-in-Oil Emulsification

- Process is not well understood
- Difficult to predict
- Occurs when water droplets are mixed into the oil
- Water content can reach 80%
- Viscosity of stable emulsions can be 1,000 times that of the fresh oil

Water-in-Oil Emulsification

- High molecular weight asphaltenes and resins act as natural surfactants
- Results when these compounds precipitate out as submicron particles
- This occurs when the lighter fractions (which serve as solvents) are lost via evaporation
- The particles orient at the water-droplet/oil interface, retarding the coaslescence of the water droplets into a separate phase.

Types of Water-in-Oil Emulsions

- Stable (30+ days)
  - 80% water; viscosity 100-1,000 x original oil
- Meso-Stable (breaks ~ 7 days)
  - 60% water; viscosity 10 x original oil

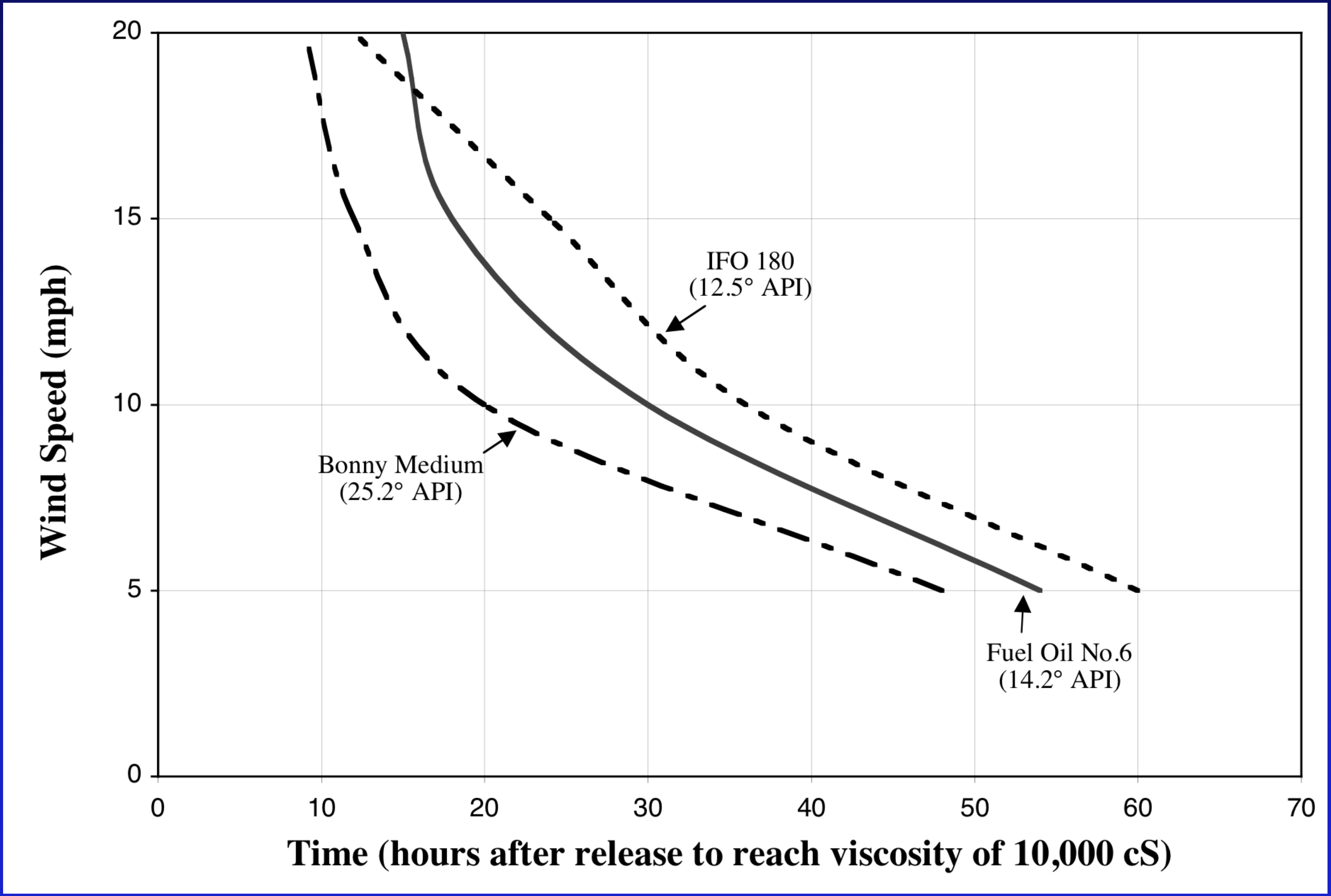
Types of Water-in-Oil Emulsions

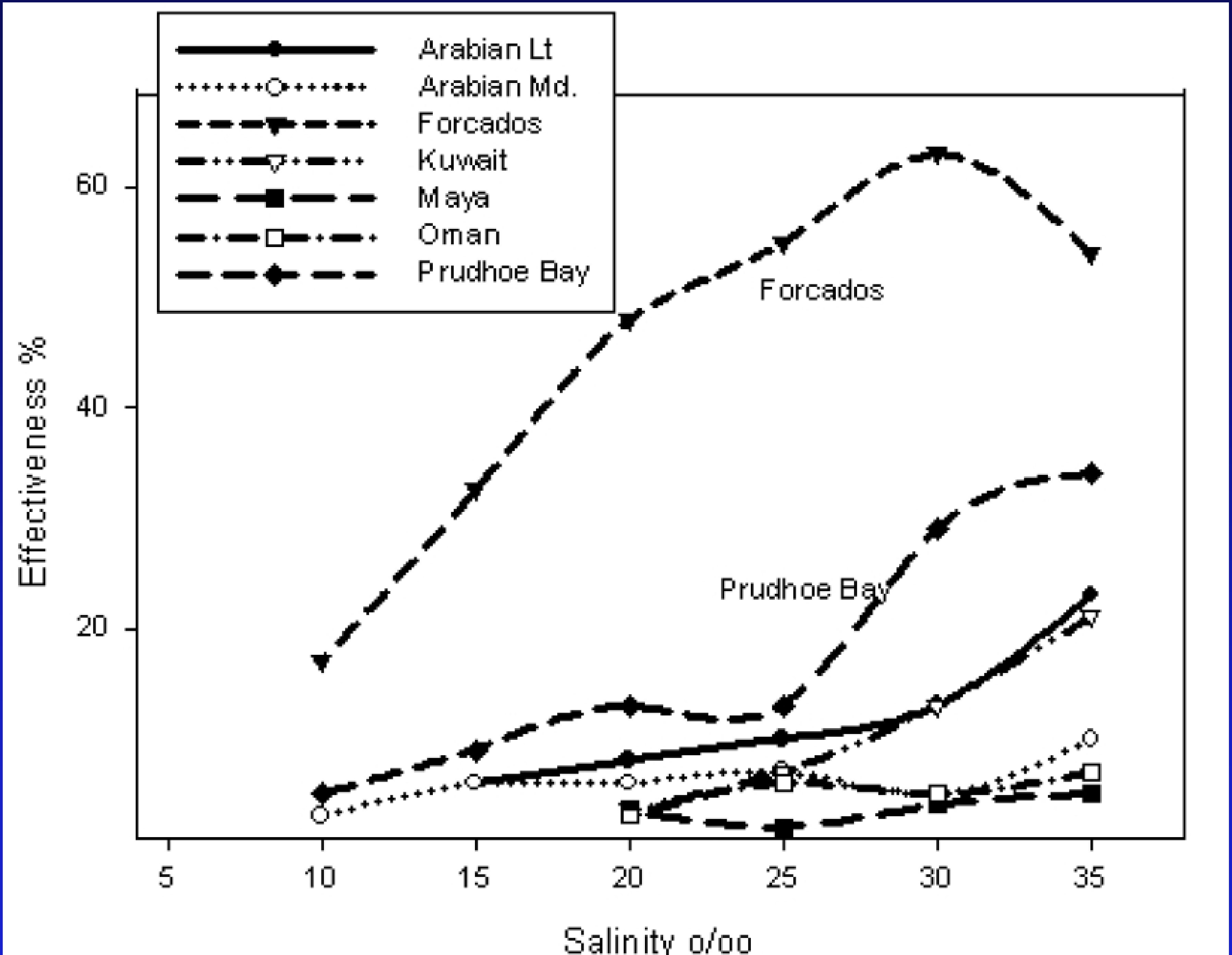
- Unstable (light refined products; heavy oils)
  - 10% water; viscosity <2 x original oil

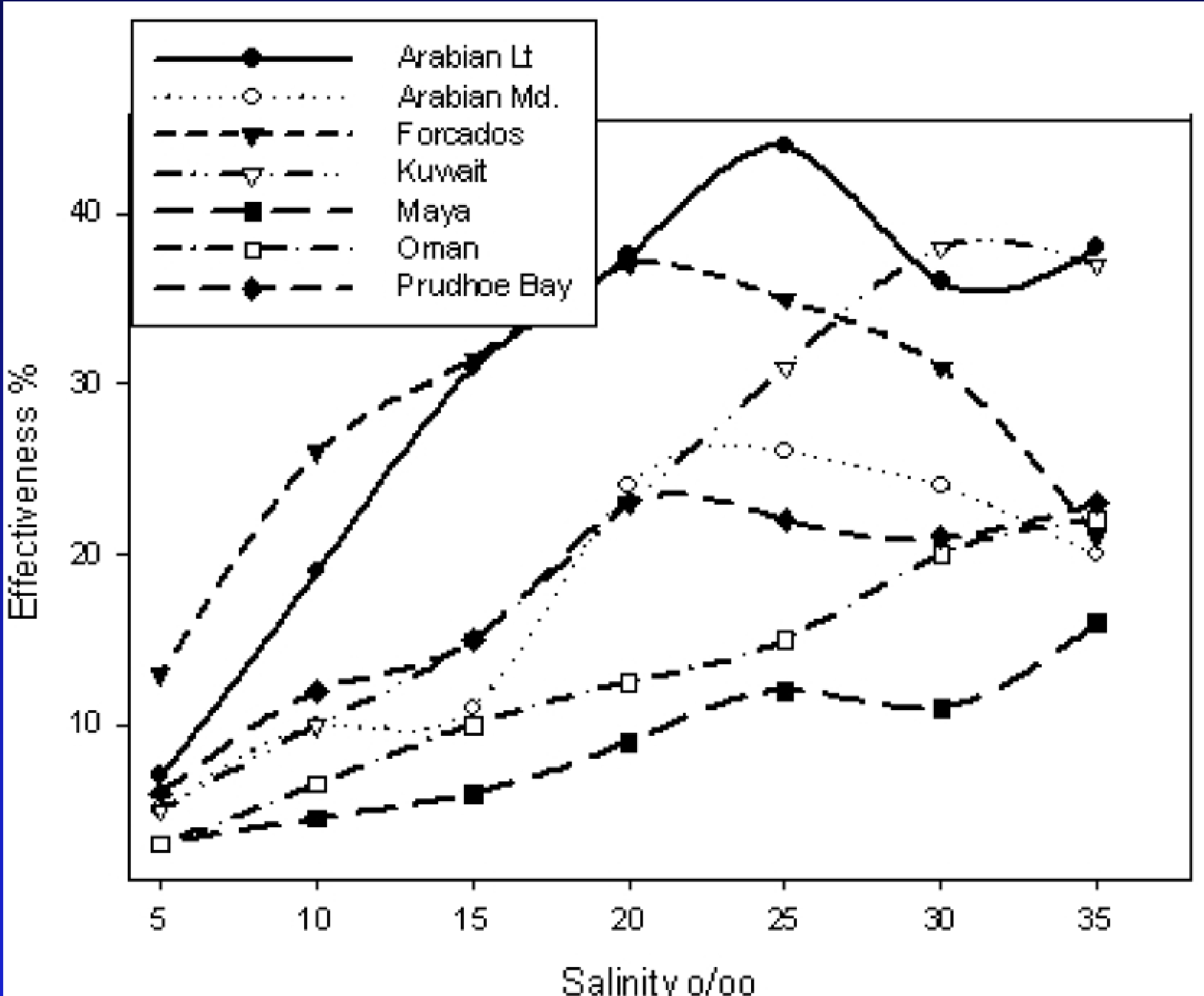
- Entrained (highly viscous oils)
  - 45% water; viscosity <2 x original oil


LOSCO RESPONSE
12/3/2000 09:38

Predicted Time to Reach Viscosity of 10,000 cS Increasing Wind Speed, 50,000 gal; 75° F




Arabian Lt
Arabian Md.
Forcados
Kuwait
Maya
Oman
Prudhoe Bay
Forcados
Prudhoe Bay
Effectiveness %
60
40
20
5
10
15
20
25
30
35
Salinity o/oo



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Salinity o/oo

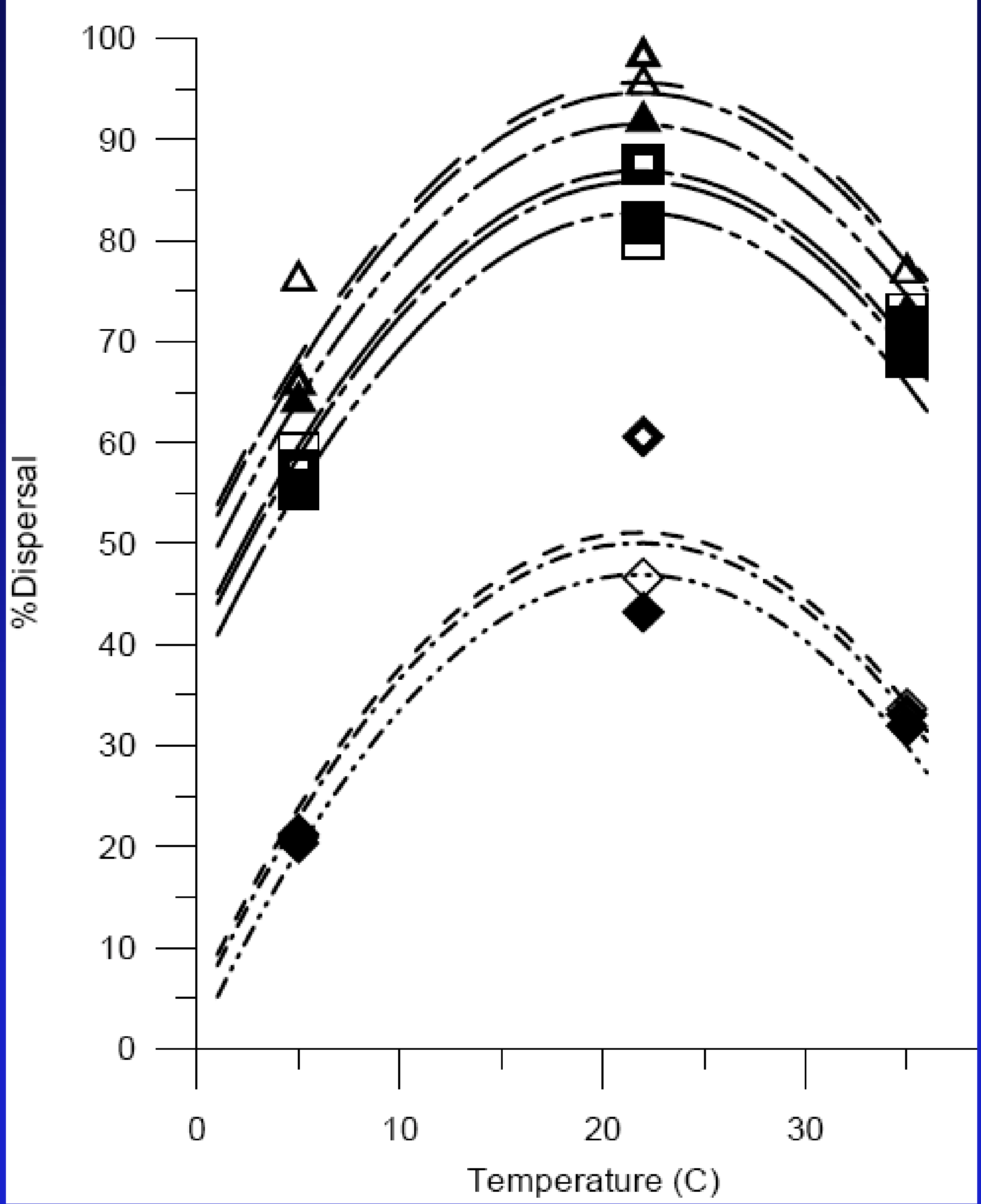
Effect of Salinity

- The hydrophilic portion of the surfactant is more soluble in water with higher salinity
- As salinity rises above a certain point (depending on the dispersant), the surfactant becomes so soluble in the water that it tends to partition completely into the water phase
- Thus, the surfactant leaves the oil drop entirely

Effect of Salinity

- Most dispersants have a very low effectiveness at 0 o/oo
- Effectiveness peaks at 20 to 40 o/oo
- Corexit 9527 is sensitive to salinity; peak ~ 25 o/oo with some oils and ~ 35 o/oo with others
- Corexit 9500 appears to be less sensitive to salinity; peaks at about 35 o/oo

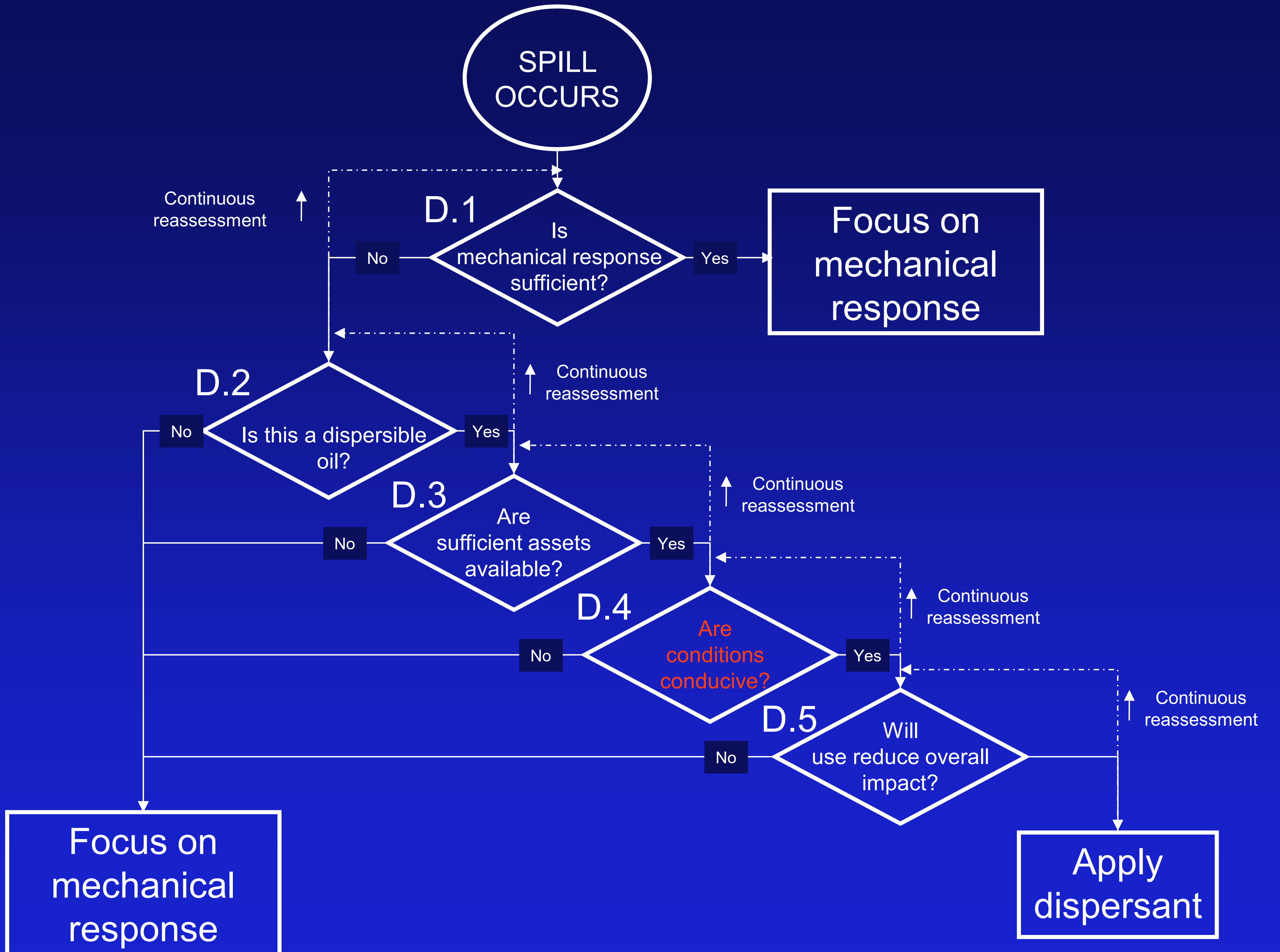
Effect of Temperature on Dispersant Effectiveness Lab Tests



NAS Report Recommendations
D.2 IS THE SPILLED OIL OR REFINED PRODUCT KNOWN TO BE DISPERSIBLE?

Identify the mechanisms and rates of oil weathering processes that control the chemical effectiveness of dispersants (bench-scale and wave-tank tests). Because of the limited funds and costs of wave-tank experiments, it is especially essential that wave-tank studies be well-coordinated.

- Measure key parameters (e.g., energy input, droplet-size distributions)
- Effectiveness on weathered emulsions is important
- Accepted standards of experimental design
- Objective is to determine relationship between energy dissipation rates and chemical effectiveness for a range of oil viscosities and weathering states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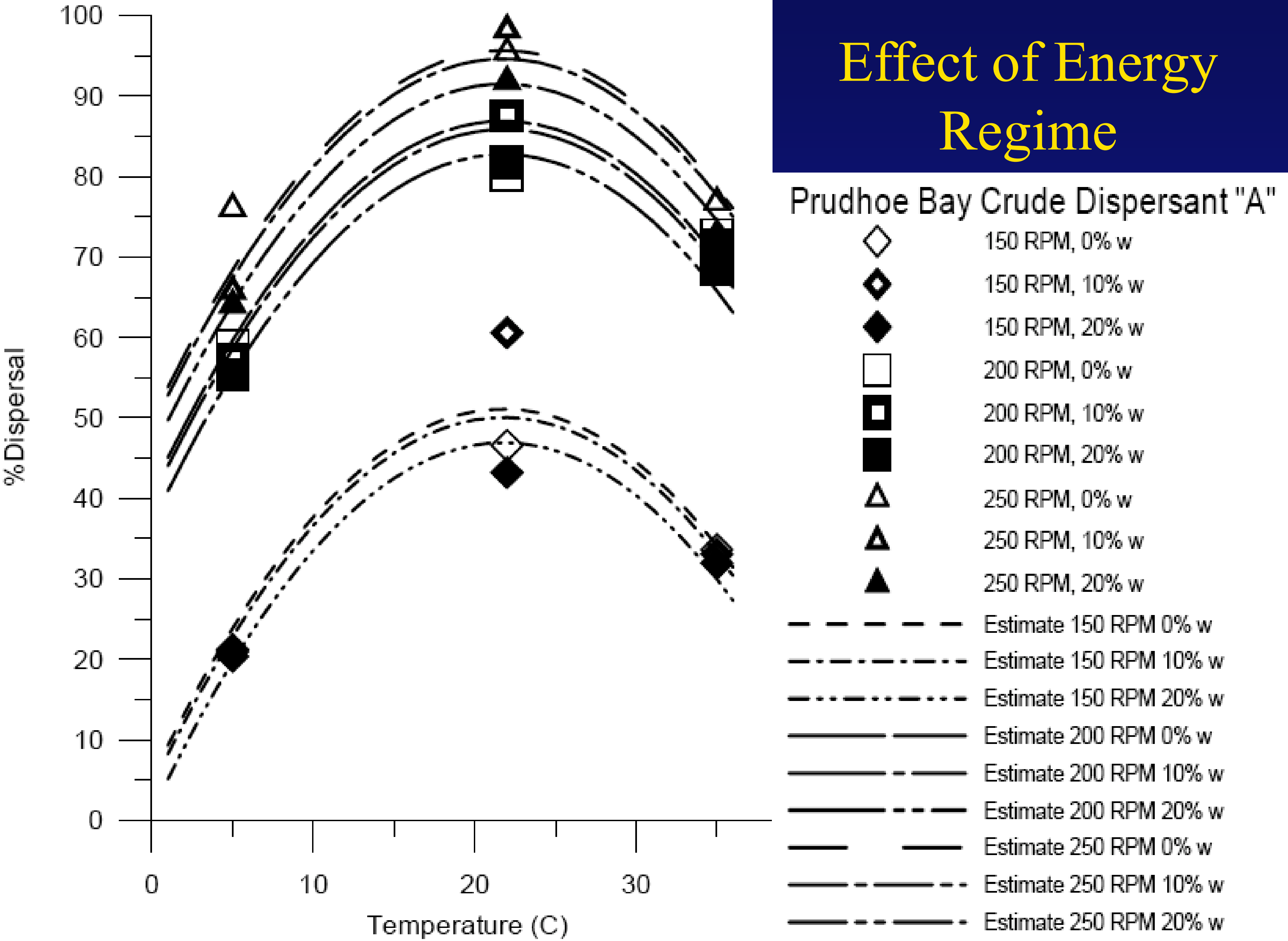
Mixing Energy Requirements

- Waves generate most of the mixing energy
- Wave energy is driven by wind
- Wind speed should be >10 kt (during or within 24 hr of application)
- Wind >25 kt, droplets will be blown off
- Can add energy by boat wake/water spray

Effect of Energy Regime



1993-94 North Sea Field Dispersant Effectiveness

Energy	Wind Speed (kt)	Oil-Dispersant	% Dispersed
Low	6	MFO	1
High	19	MFO	2
High	19	MFO-1100x	10
High	19	MFO-SG	17
High	19	MFO-OSR5	30

1993-94 North Sea Field Dispersant Effectiveness

Energy	Wind Speed (kt)	Oil-Dispersant	% Dispersed
High	14	MFO	4
Low	10	MFO-SG	8
High	12	MFO-SG	16
High	14	MFO-9527	26

1993-94 North Sea Field Dispersant Effectiveness

Energy	Wind Speed (mph)	Oil-Dispersant	% Dispersed
High	16	Forties	5
High	13	Forties-SG	16

NAS Report Recommendations
D.4 ARE THE ENVIRONMENTAL CONDITIONS CONDUCIVE?

Develop a research program that provides the data needed to predict, through modeling of the chemical, environmental, and operational conditions, the overall effectiveness of a dispersant application, specifically considering conditions representative of nearshore physical settings.

- Models provide quantitative predictions of tradeoffs with/without dispersants
- Use in pre-planning and emergency response
- **Effectiveness currently an input value**
- Complex combination of chemical, operational, and hydrodynamic factors
- Need ability to predict effectiveness over time using physical-chemical models (determine the window of opportunity)
- Key consideration in tradeoff analyses

NAS Report Recommendations
D.4 ARE THE ENVIRONMENTAL CONDITIONS CONDUCIVE?

Experimental systems used for bench-scale effectiveness tests should be characterized to determine the energy dissipation rates that prevail over a wide range of operating conditions. Future effectiveness tests should measure chemical effectiveness over a range of energy dissipation rates to characterize the functional relationship between these variables. Finally, evaluation of chemical effectiveness should always include measurement of the droplet-size distribution of the dispersed oil.

- Energy dissipation rate is the most important hydrodynamic factor in predicting dispersion
- It varies widely among experimental systems but is seldom measured
- Droplet size distributions in experimental systems are needed to identify mechanisms and compare them to those observed at sea

NAS Report Recommendations
D.4 ARE THE ENVIRONMENTAL CONDITIONS CONDUCIVE?

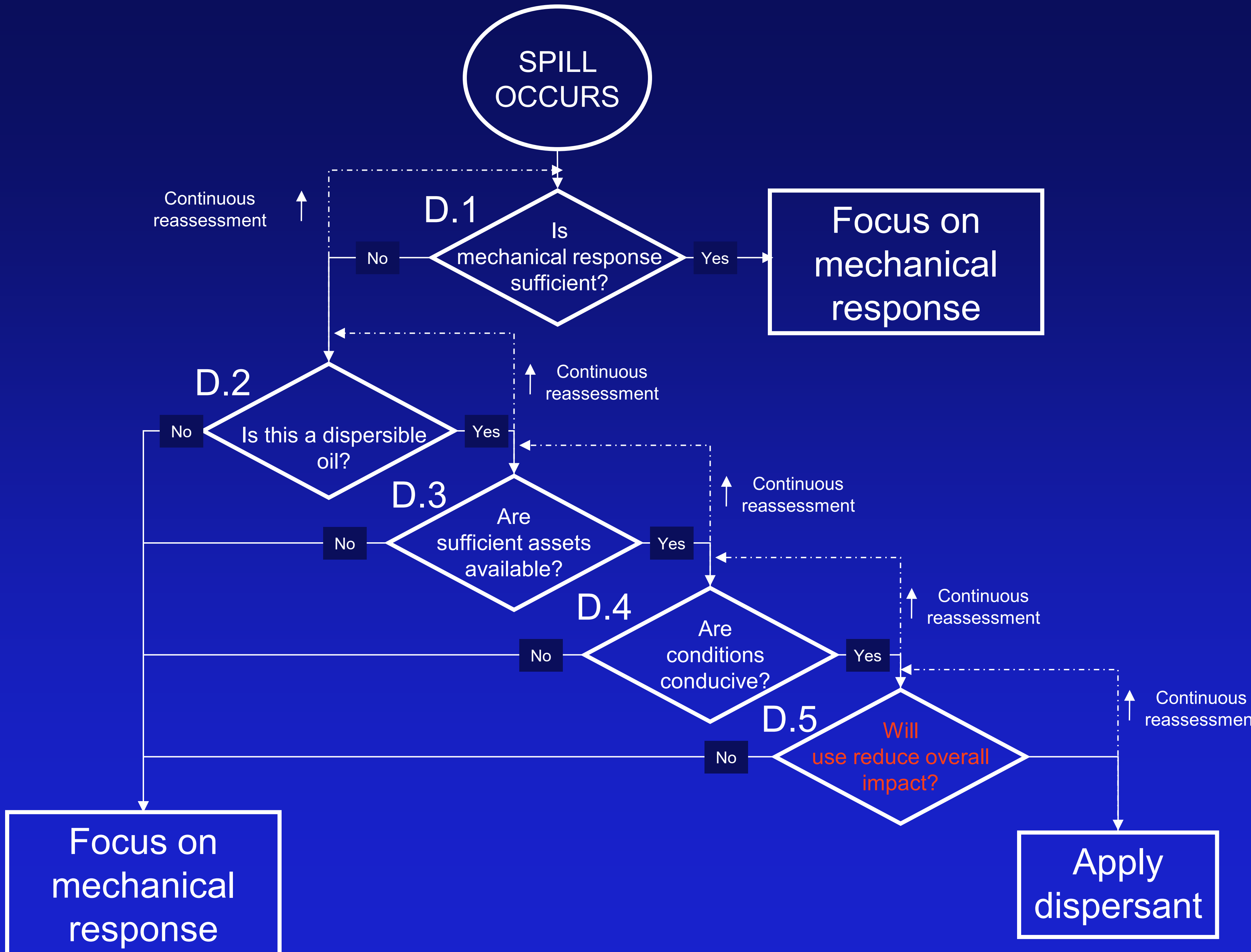
The design of wave-tank dispersant-effectiveness studies should specifically test hypotheses regarding factors that can affect operational effectiveness.

- Wave-tanks tests are more realistic - mechanism of energy input and droplet formation
- Operational factors to consider:
  - water-in-oil emulsification
  - formation of a "skin" that resists dispersant penetration
  - dispersant droplet size and impact velocities
  - range of energy-dissipation rates

NAS Report Recommendations
D.4 ARE THE ENVIRONMENTAL CONDITIONS CONDUCIVE?

Develop a coordinated program to obtain needed information about turbulence regimes at a variety of interrelated scales.

- To correlate lab-scale and mesocosm experiments with open-ocean conditions - need understanding of the turbulence regime in all three
- Biggest uncertainty in computer models is appropriate horizontal and vertical diffusivities
- Growing availability of OOS in coastal waters will improve real-time modeling applications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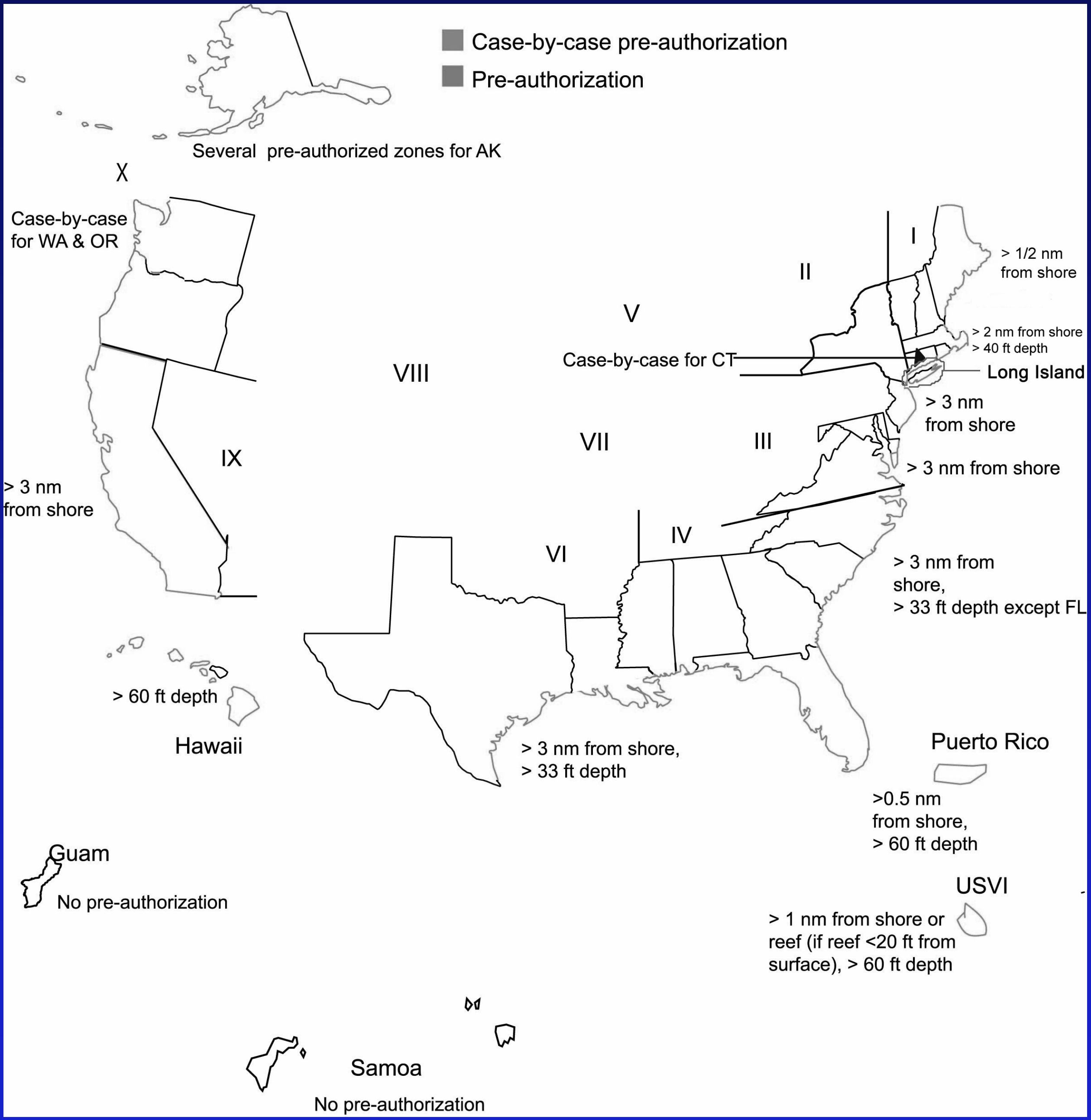
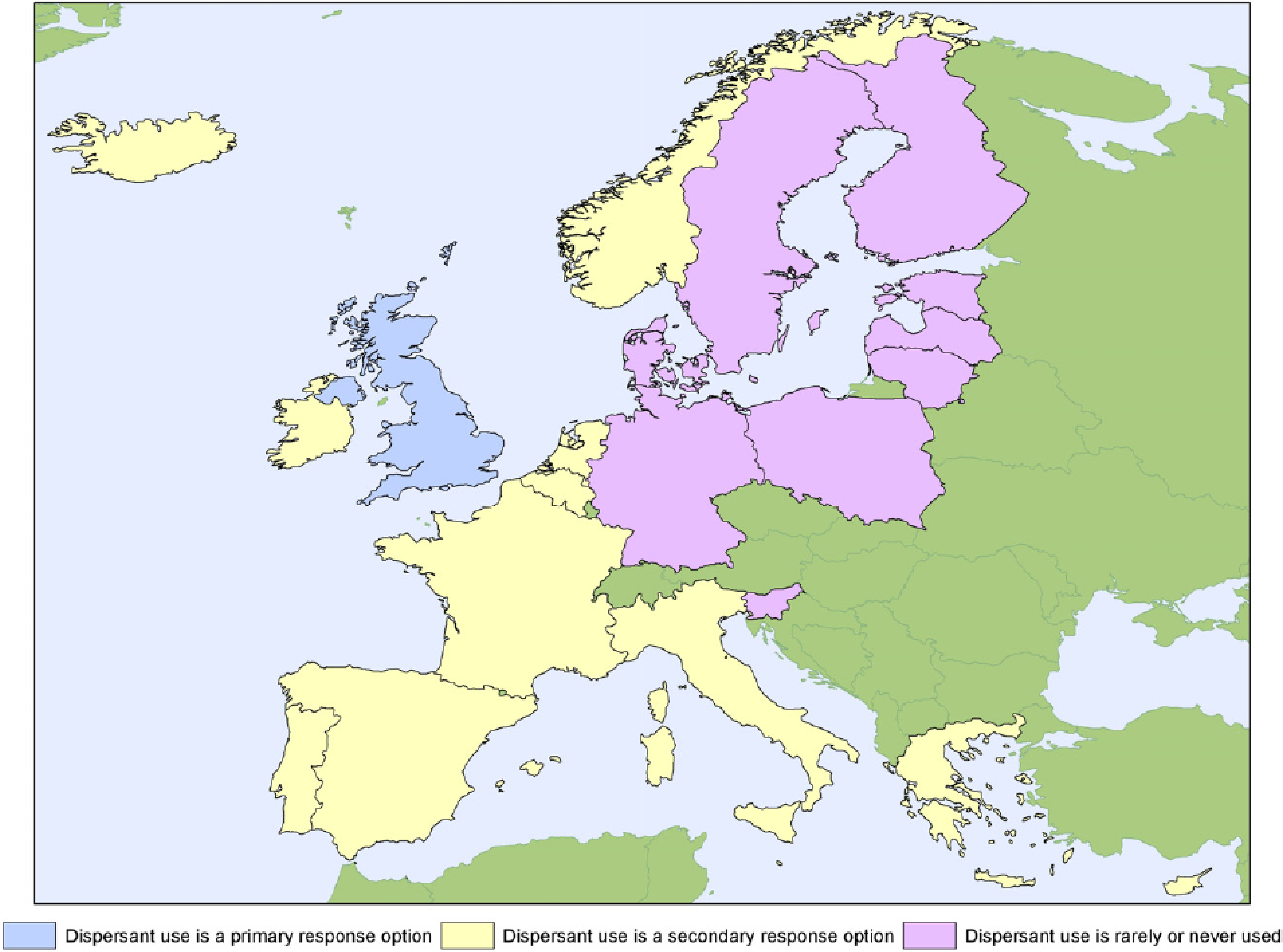
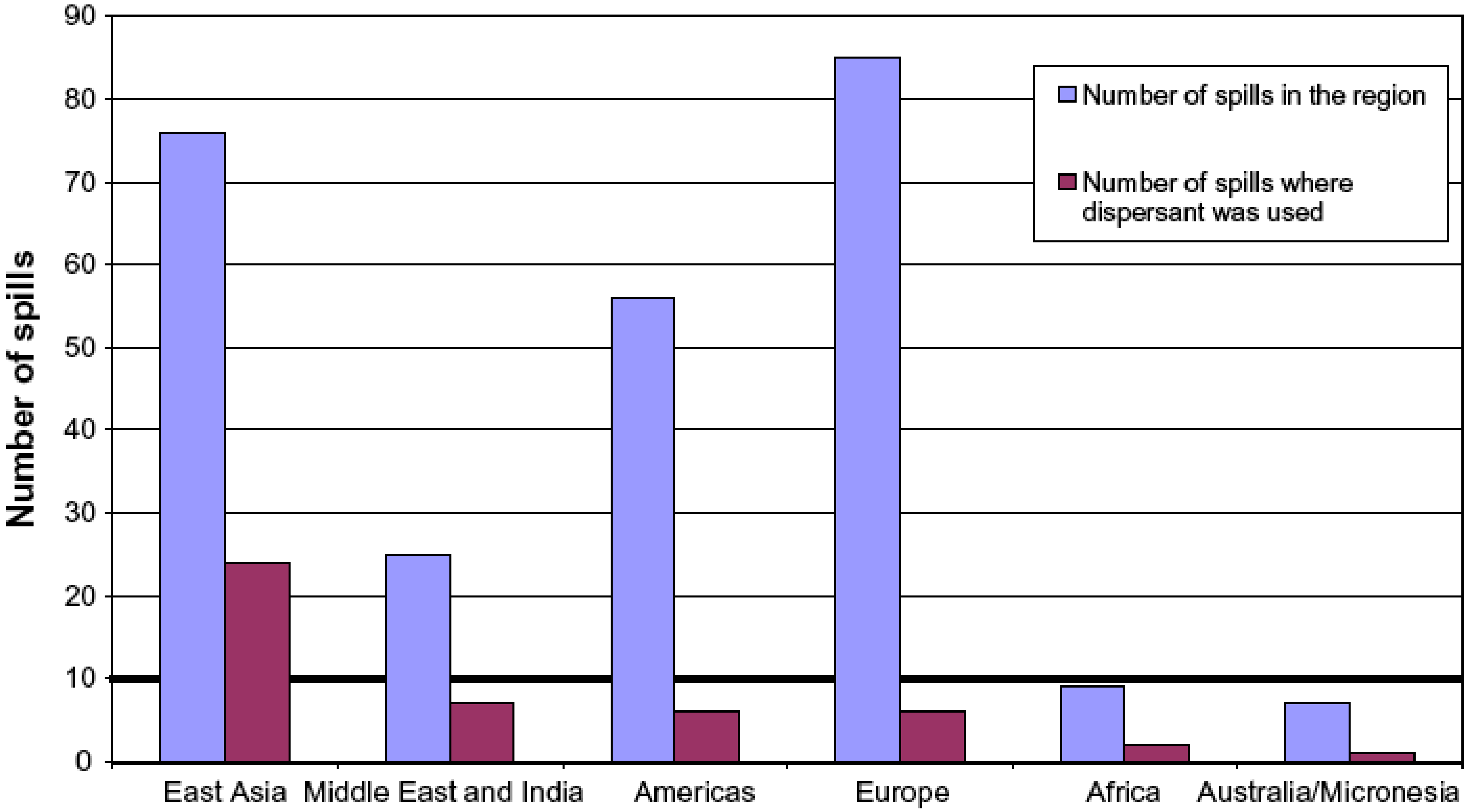


Case-by-case pre-authorization
Pre-authorization
Several pre-authorized zones for AK
X
Case-by-case for WA & OR
> 3 nm from shore
IX
VIII
VII
VI
V
Case-by-case for CT
II
I
> 1/2 nm from shore
> 2 nm from shore
> 40 ft depth
Long Island
> 3 nm from shore
III
> 3 nm from shore
IV
> 3 nm from shore, > 33 ft depth except FL
> 3 nm from shore, > 33 ft depth
> 60 ft depth
Hawaii
Puerto Rico
>0.5 nm from shore, > 60 ft depth
USVI
> 1 nm from shore or reef (if reef <20 ft from surface), > 60 ft depth
Guam
No pre-authorization
Samoa
No pre-authorization


Dispersant use is a primary response option
Dispersant use is a secondary response option
Dispersant use is rarely or never used

Use of Dispersants: 258 Spills Responded to by ITOPF 1995-2005



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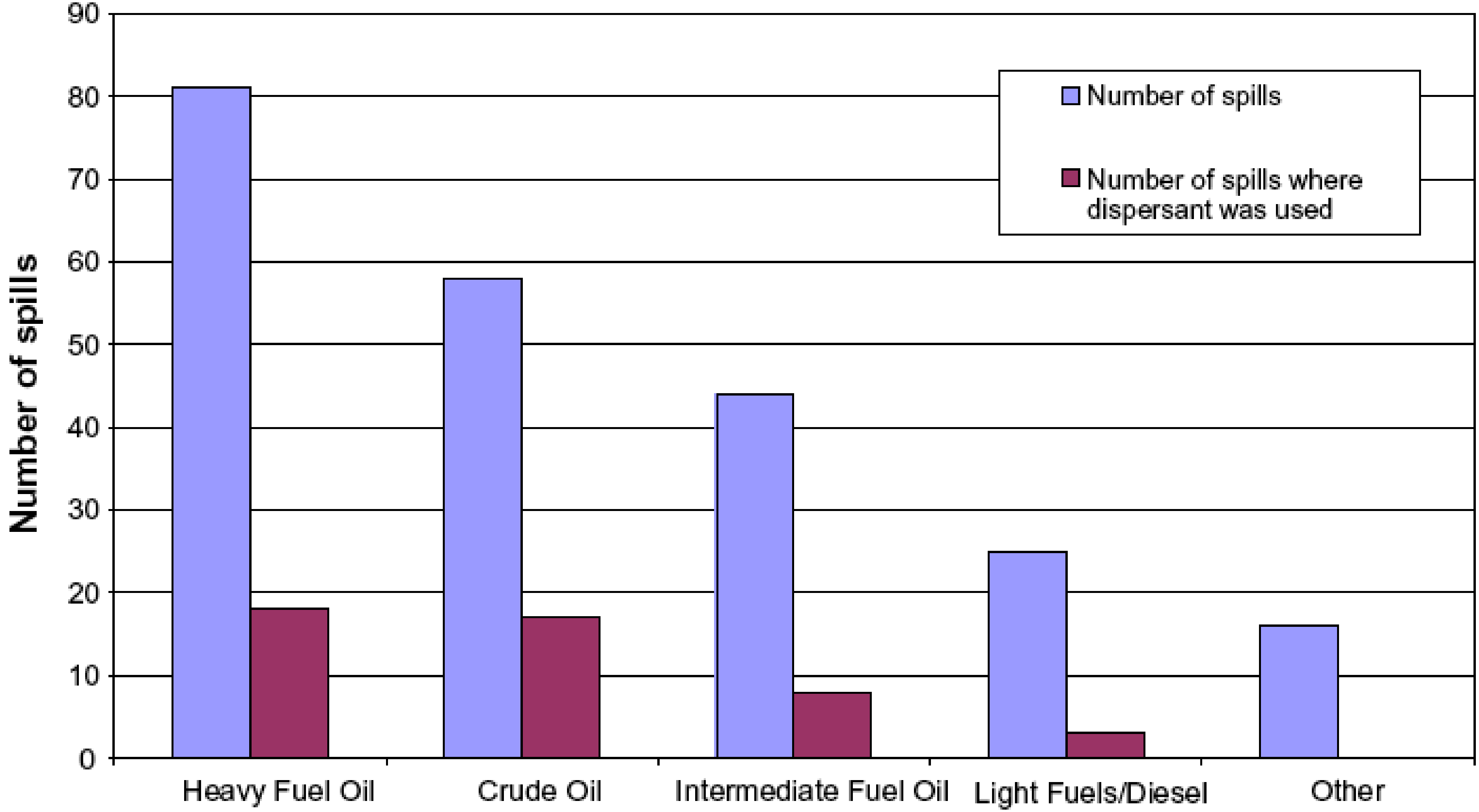
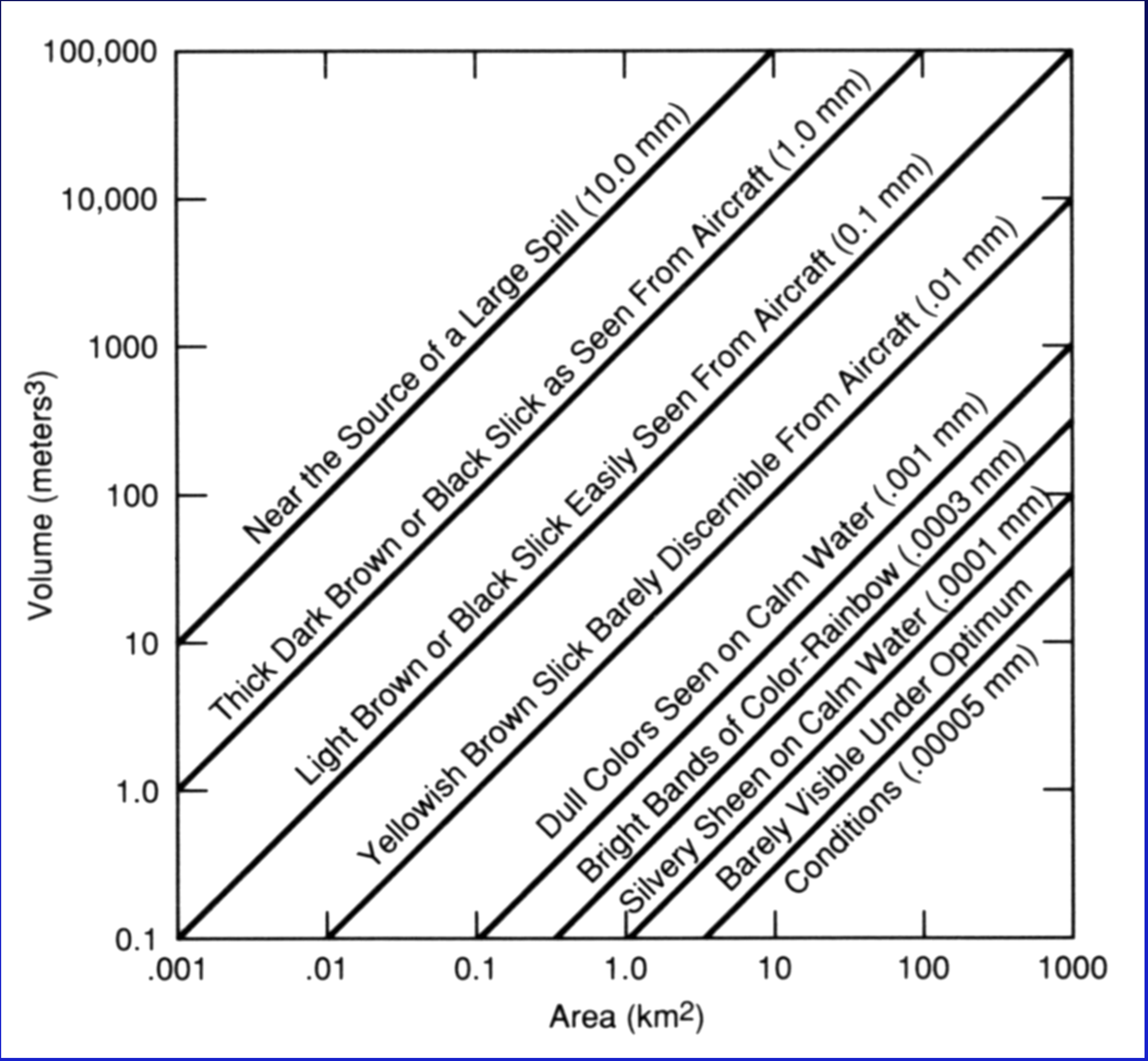
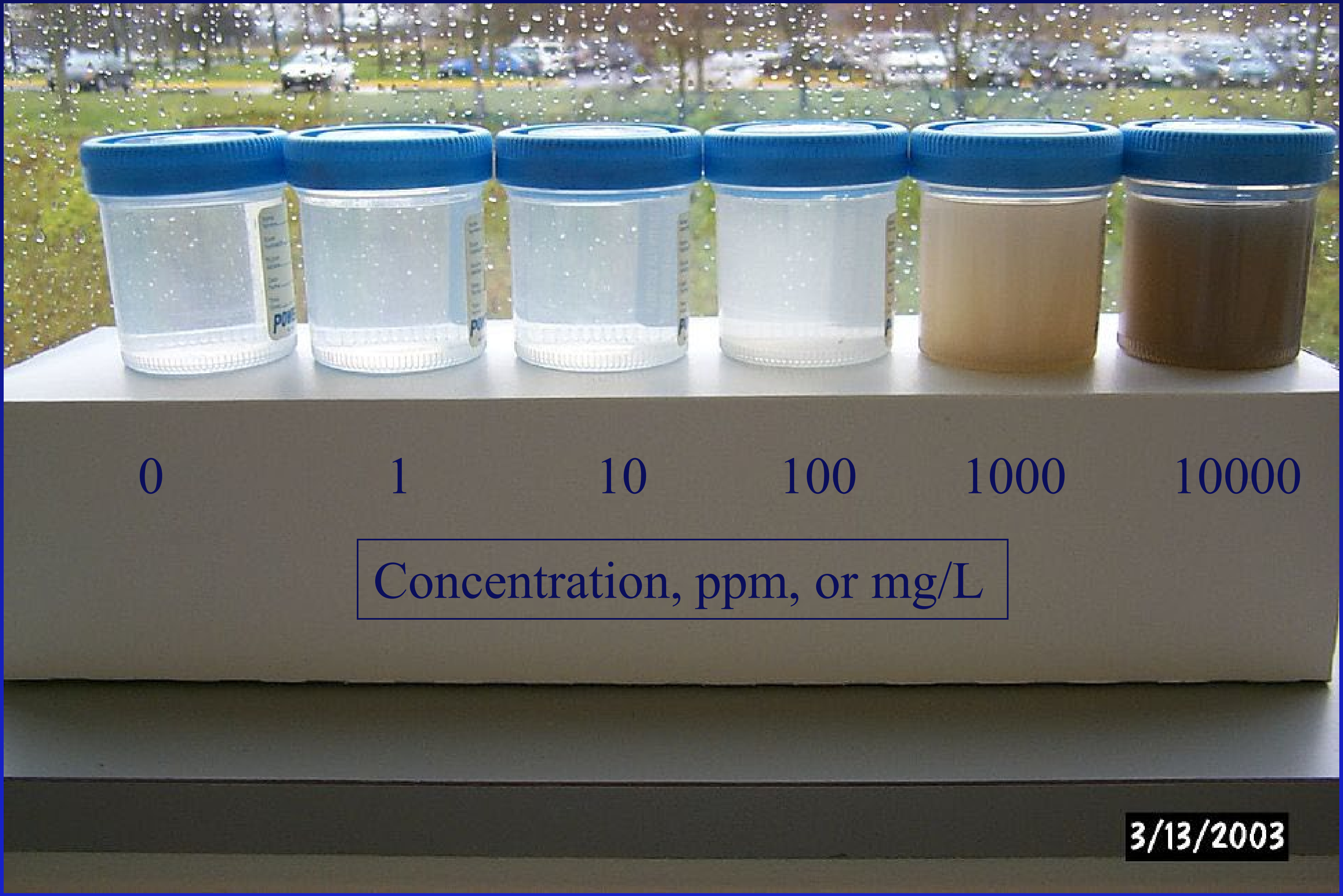



100,000
10,000
1000
100
10
1.0
0.1
Volume (meters3)
.001
.01
0.1
1.0
10
100
1000
Area (km2)
Near the Source of a Large Spill (10.0 mm)
Thick Dark Brown or Black Slick as Seen From Aircraft (1.0 mm)
Light Brown or Black Slick Easily Seen From Aircraft (0.1 mm)
Yellowish Brown Slick Barely Discernible From Aircraft (.01 mm)
Dull Colors Seen on Calm Water (.001 mm)
Bright Bands of Color-Rainbow (.0003 mm)
Silvery Sheen on Calm Water (.0001 mm)
Barely Visible Under Optimum Conditions (.00005 mm)


0
1
10
100
1000
10000
Concentration, ppm, or mg/L
3/13/2003