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How Oil Dispersants Work

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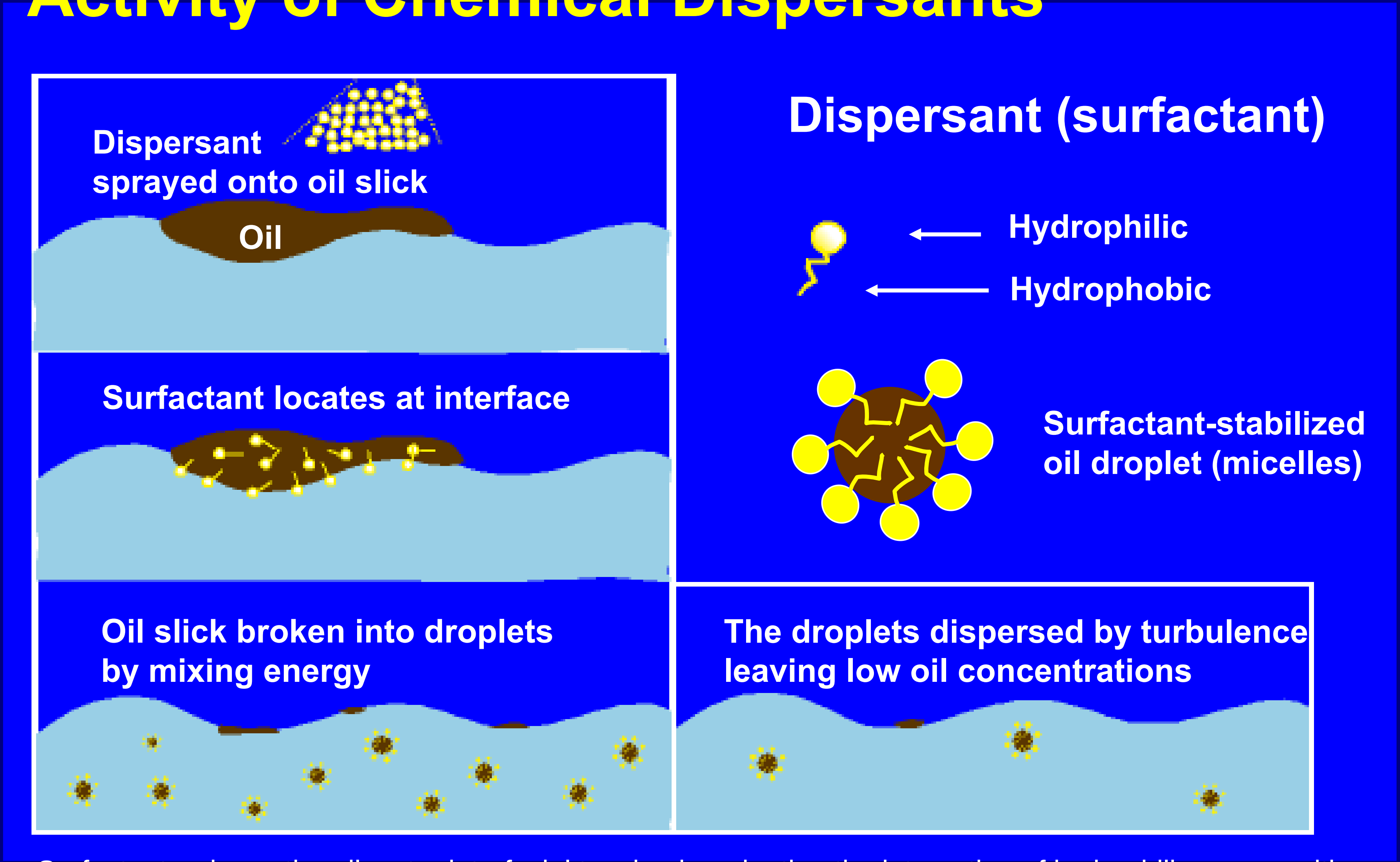
What Are Dispersants?

- Dispersants are liquid solutions of detergent-like surfactants dissolved or suspended in solvent
- The surfactants have two ends: one attracted to oil (lipophilic) and another attracted to water (hydrophilic)

- The solvent enables the surfactants (active ingredients) to be applied and helps get them through the oil film to the water interface
- At the interface the surfactants reduce the surface tension allowing the oil to enter the water as tiny droplets which are degraded by natural bacteria

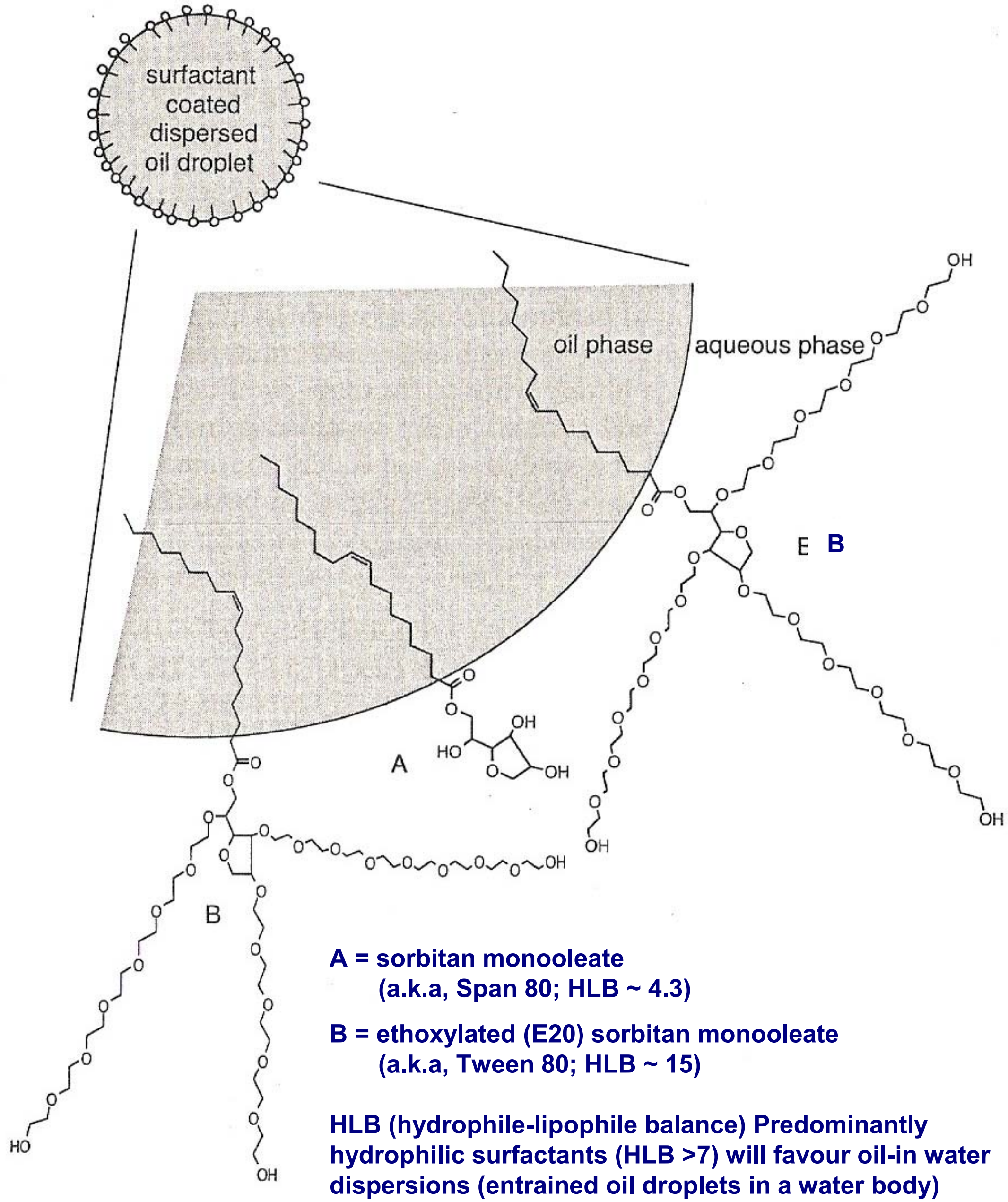
Activity of Chemical Dispersants



Surfactant reduces the oil-water interfacial tension by orienting the interaction of hydrophilic groups with the water phase and the hydrophobic groups with oil

Reduced oil-water interfacial tension facilitates the formation of a large number of small oil droplets that can be entrained in the water column

Orientation of surfactants at oil water interface in dispersed oil droplets



A = sorbitan monooleate
(a.k.a, Span 80; HLB ~ 4.3)

B = ethoxylated (E20) sorbitan monooleate
(a.k.a, Tween 80; HLB ~ 15)

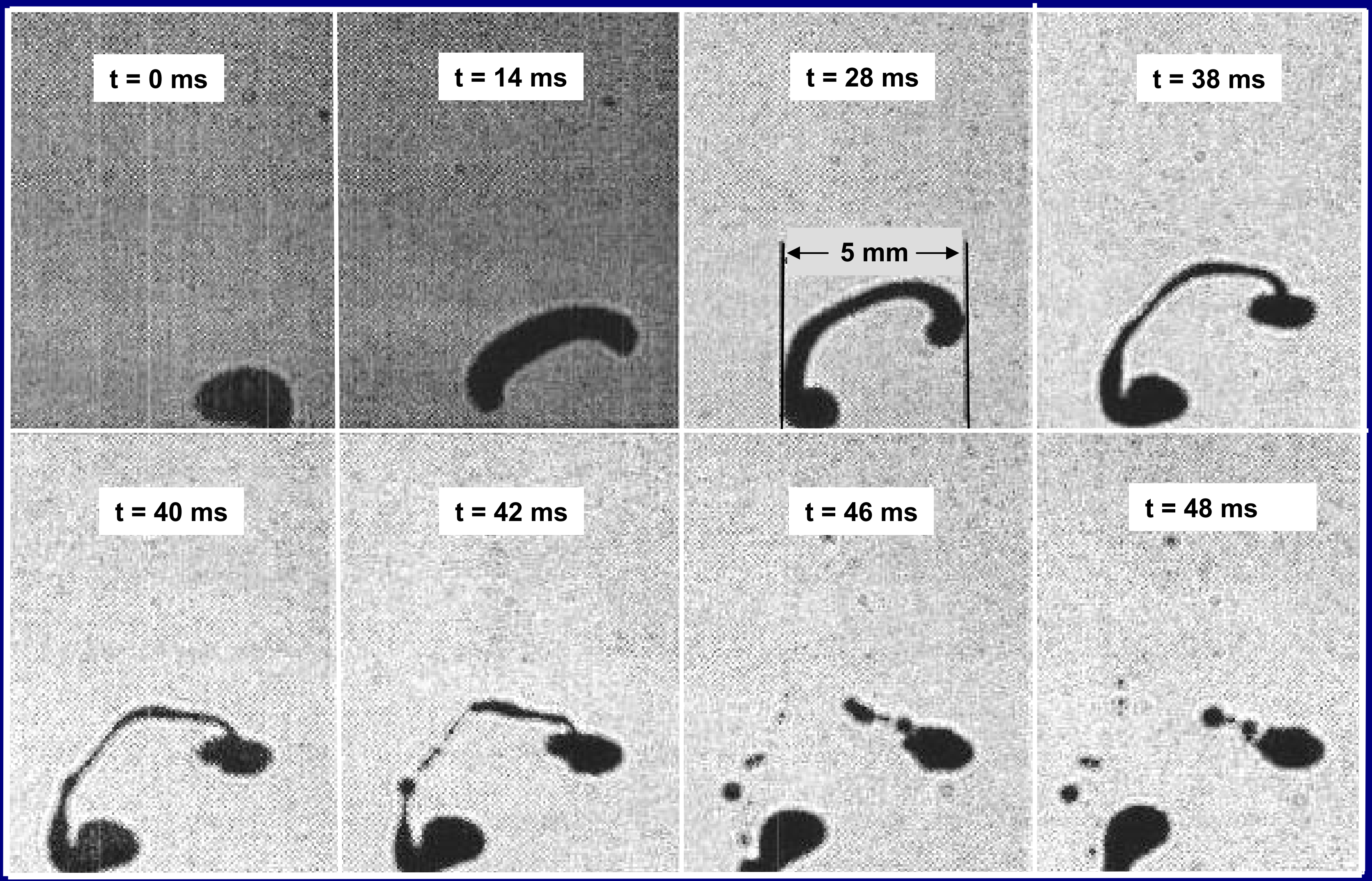
HLB (hydrophile-lipophile balance) Predominantly hydrophilic surfactants (HLB >7) will favour oil-in water dispersions (entrained oil droplets in a water body)

Chemical Constituents (Dispersant – Corexit)

CAS #	Name	Common Day-to-Day Use Examples
1338-43-8	Sorbitan, mono-(9Z)-9-octadecenoate	Skin cream, body shampoo, emulsifier in juice
9005-65-6	Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs.	Baby bath, mouth wash, face lotion, emulsifier in food
9005-70-3	Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs.	Body/Face lotion, tanning lotions
577-11-7	* Butanedioic acid, 2-sulfo-, 1,4-bis(2-ethylhexyl) ester, sodium salt (1:1)	Wetting agent in cosmetic products, gelatin, beverages
29911-28-2	Propanol, 1-(2-butoxy-1-methylethoxy)	Household cleaning products
64742-47-8	Distillates (petroleum), hydrotreated light	Air freshener, cleaner
111-76-2	** Ethanol, 2-butoxy	Cleaners

*** Contains 2-Propanediol**
**** Ethanol, 2-butoxy-) is absent in the composition of COREXIT 9500**

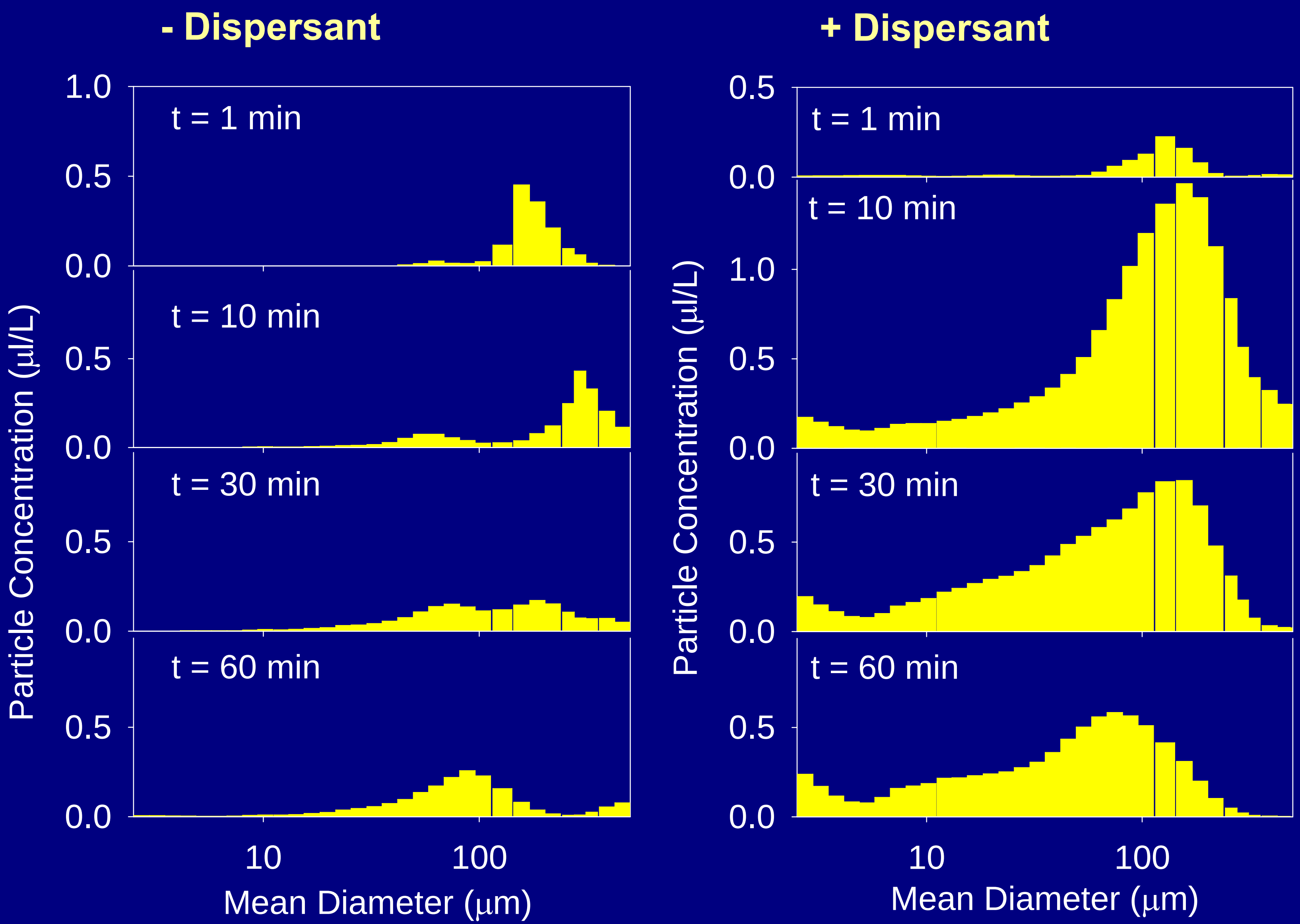
Dispersant Activity



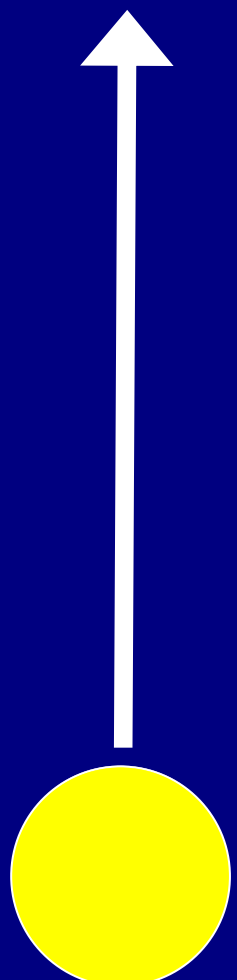
Extracted images from cinematic digital holography of turbulent break-up of crude oil mixed with dispersants into microdroplets

Gopalan, B. and J. Katz (2010) Physical Review Letters 104, 054501

Oil Droplet Size Distribution



Small Oil Droplets Rise Slower than Large Oil Droplets



STOKES LAW

$$\Delta h / t = \frac{D^2(\rho_w - \rho_o)g}{18\eta_w}$$

Where: *$\Delta h / t$ = rise velocity*

D = drop diameter

ρw = aqueous density

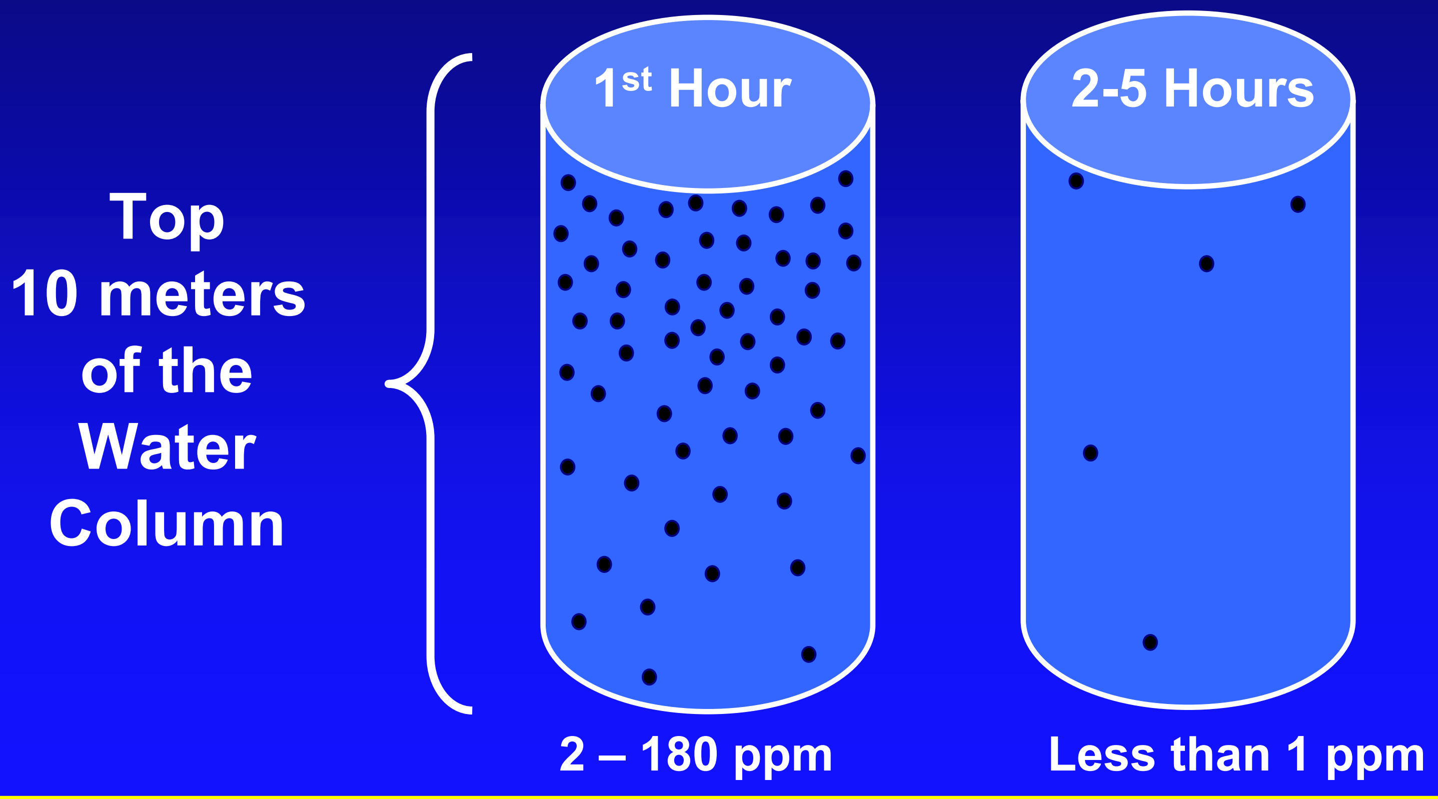
ρo = oil density

g = gravitational constant

ηw = aqueous viscosity

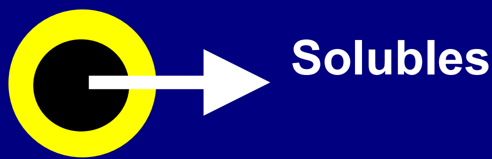
Dispersion of Oil

In the open sea currents distribute oil over a large area

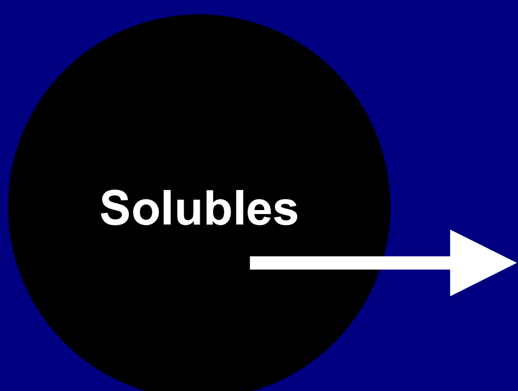


Oil is diluted to concentrations below toxicity threshold limits

Fate of Oil Components in Oil Droplets Entrained in the Water Column



20µm oil droplet surrounded by surfactant molecules
(Area 5×10^{3} Volume 3.3×10^{4})



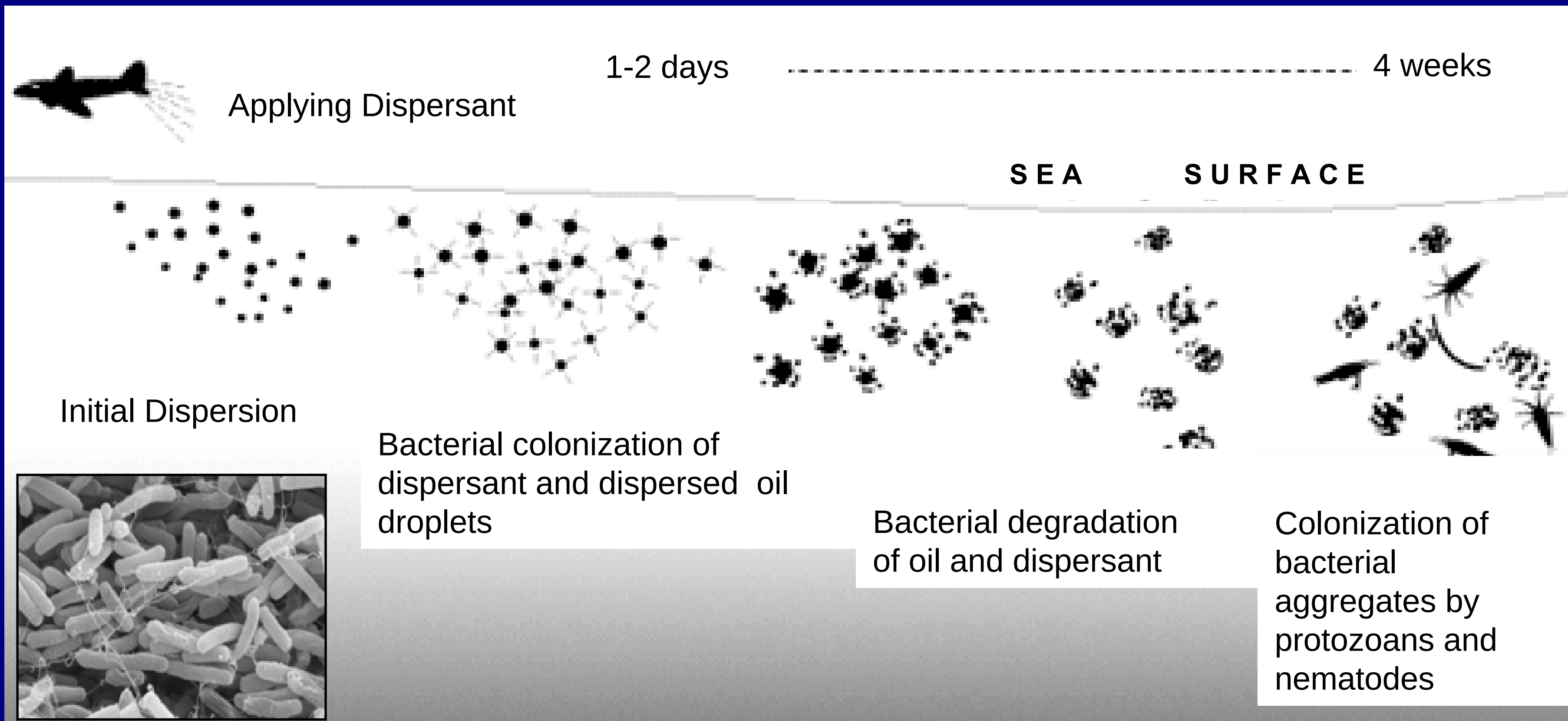
2000µm entrained oil droplet
(Area 5×10^{7} Volume 3.3×10^{10})

Rate of loss of volatile and water soluble components (chemical partitioning) and microbial degradation are influenced by surface-to-volume ratios

Sphere surface area: $4 \pi r^2$
Sphere volume: $4/3 \pi r^3$

For two orders of magnitude
Increase in diameter:
Surface area increases by 10,000x
Volume increases by 1,000,000x

Fate of Dispersed Oil Droplets

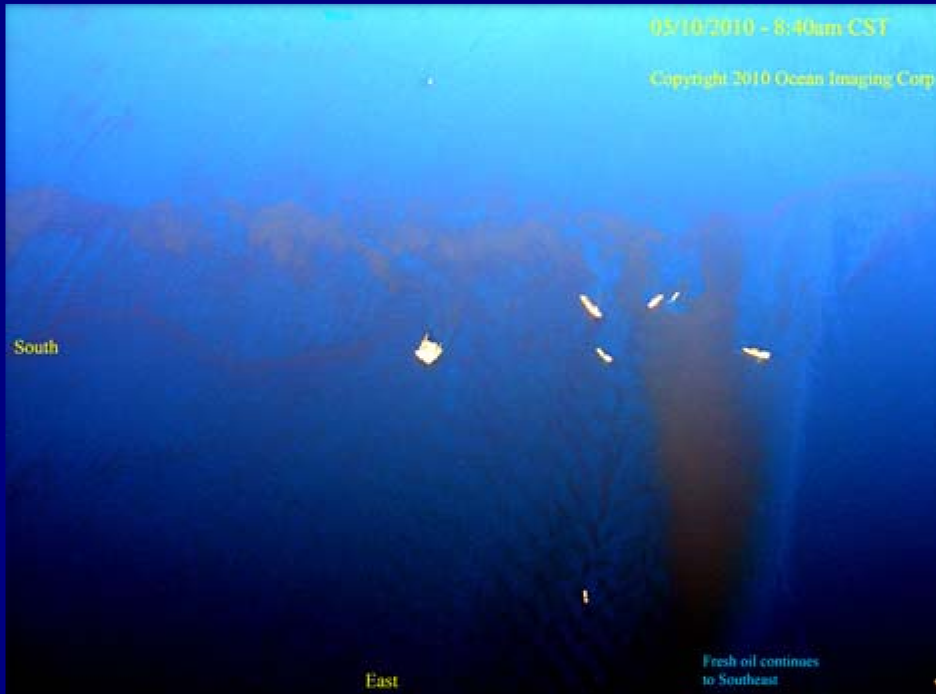


Source: *http://www.response.restoration.noaa.gov*

Application of Oil Dispersants

- In addition to (mechanical recovery techniques (skimming and booming) and in situ burning, oil dispersants were used to prevent landfall of the oil in the Deepwater Horizon Spill

- Beginning in early May responders began injecting dispersants at the source of the release (~1500m depth) to reduce oil from reaching the surface
  - Advantages of subsurface injection:
    - Reduced VOCs (volatile organic compounds)
    - Reduced Oil Emulsification
    - Volume of dispersant needed


05/10/2010 - 8:40am CST
Copyright 2010 Ocean Imaging Corp
South
East
Fresh oil continues
to Southeast

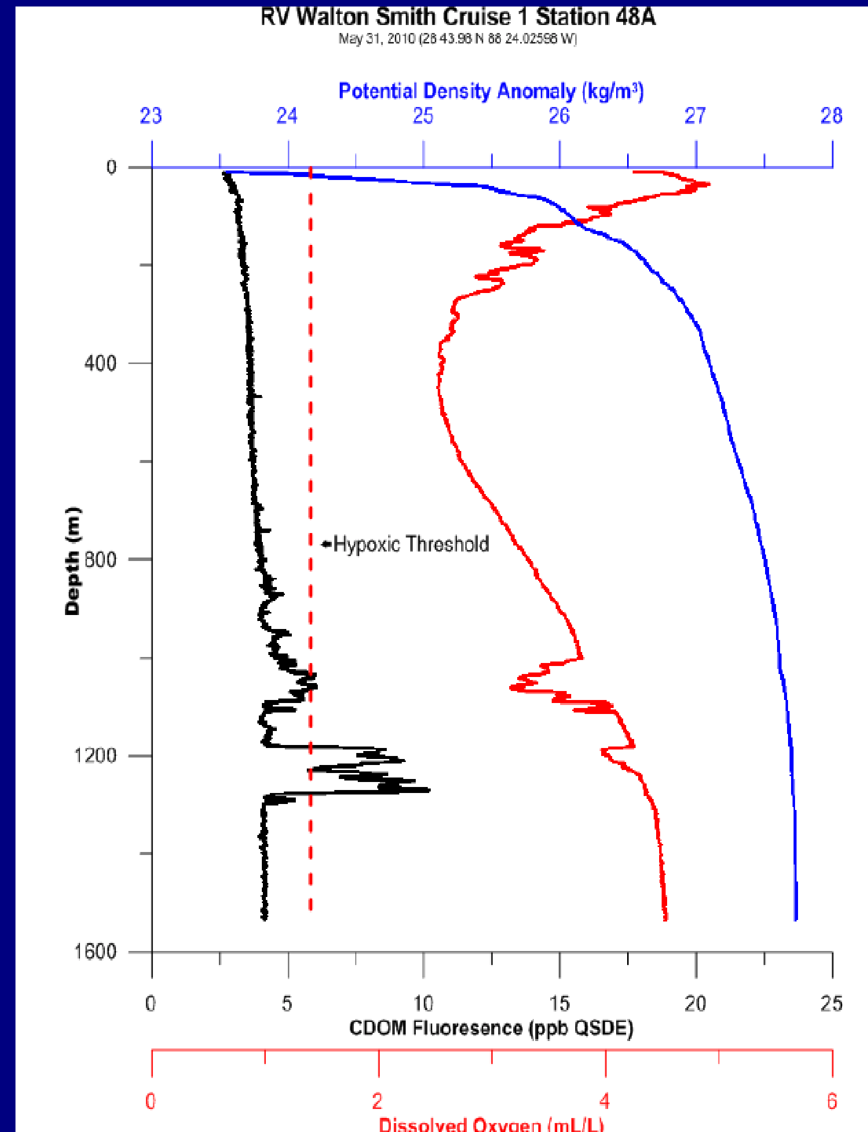
Dispersant Monitoring and Assessment for Subsurface Dispersant Application

- Directive issued by US EPA and USCG required BP to implement a monitoring and assessment plan for subsurface and surface use of dispersants
  - Shutdown Criteria
    - Significant reduction in dissolved oxygen (< 2 mg/L)
    - Rotifer acute toxicity tests
- Later addenda to implement SMART Tier 3 Monitoring Program
  - Droplet size distribution (LISST)
  - CTD instrument equipped with CDOM fluorometer
  - Discreet sample collection to measure fluorometry (FIR)
  - Eliminate surface application altogether
  - Subsea limited to < 15,000 gpd

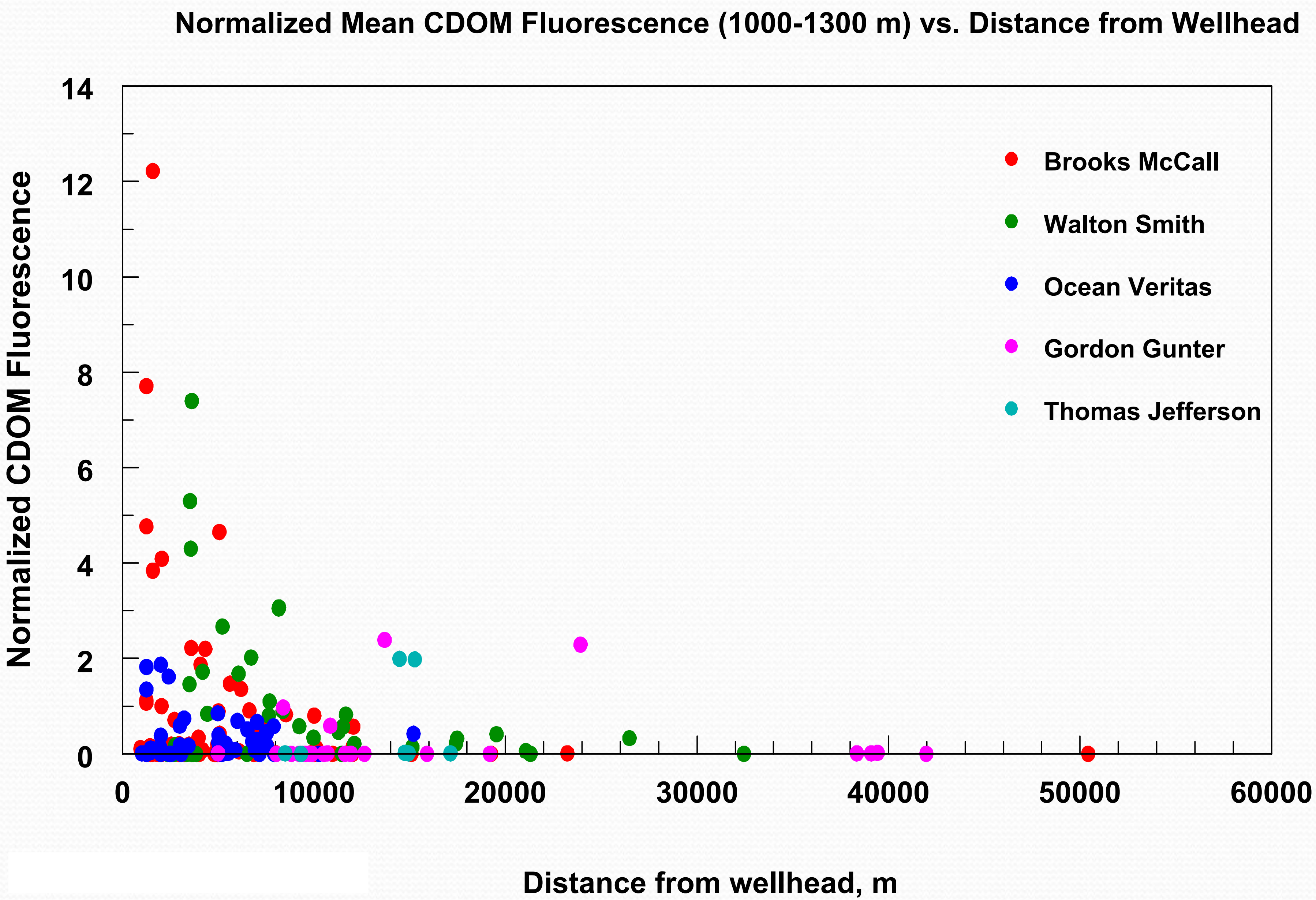
Joint Analysis Group (JAG) for Surface and Subsurface Oceanographic, Oil, and Dispersant Data

- Working group of scientists from EPA, NOAA, OSTP and DFO
- Analyze an evolving database of sub-surface oceanographic data by BP, NOAA, and academic scientists
- Near term actions:
  - Integrate the data
  - Analyze the data to describe the distribution of oil and the oceanographic processes affecting its transport
  - Issue periodic reports

Vertical Profile of O_2 Depressions Coincident with Fluorescence Peaks



CDOM (Colored Dissolved Organic Matter Fluorescence)



Preliminary Conclusions

- Fluorometry shows recurring anomaly at 1000 to 1300 m
  - Strongest near wellhead, decreases with distance
  - Trending WS to NE direction consistent with water movement along isobath isobath
  - Natural Organic Matter contribute to fluorescence signal
  - Spatial and temporal variability in fluorometric anomalies
  - Active natural seeps mapped ~12 km SW and 17 km NE of wellhead
  - Minimum detection limit of CDOM fluorometers ~1 ppm oil
- CTD DO anomalies seen at 1000 to 1300 m
  - Interpretation to be refined and data validated by Winkler O_2 titrations against electronic sensor data