Effects of oil dispersants on the environmental fate, transport and distribution of spilled oil in marine ecosystems

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Outline

- Roles of dispersants on sediment retention of oil compounds
- Effects of dispersants on settling of suspended sediment particles and transport of oil compounds
- Effects of dispersants and oil on formation of marine oil snow

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Part I. Effects of Oil Dispersants on Sediment Retention of Polycyclic Aromatic Hydrocarbons in the Gulf Coast Ecosystems

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Gong et al. Environmental Pollution 185 (2014) 240-249

Application of Oil Dispersants

- In the 2010 the DWH oil spill, BP applied ~2.1 MG of oil dispersants (Kujawinski et al., 2011)
  - Corexit 9500A and Corexit 9527A
- About 1.1 MG injected at the wellhead (pressure = 160 atm, temperature = 4 ^oC) (Thibodeaux et al., 2011)
- Consequently, ~770,000 barrels (or ~16%) of the spilled oil were dispersed (Ramseur, 2010)

Kujawinski, E.B. et al. (2011) *Environ. Sci. Technol.*, 45, 1298-1306.
Ramseur, J.L. (2010) www.crs.gov, R41531.

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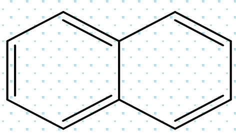
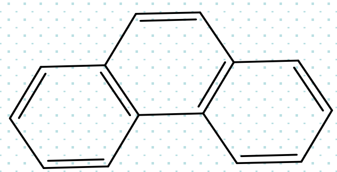
Polycyclic Aromatic Hydrocarbons (PAHs) in Spilled Oil

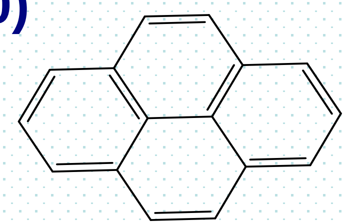
- **A class of principal persistent oil components**
  - **The Macondo well oil contained ~3.9% PAHs by weight, and ~21,000 tons of PAHs were released during the 2010 spill (Reddy et al., 2011)**
  - **PAHs are toxic, mutagenic, carcinogenic and persistent**
- **Elevated concentrations of PAHs were reported during the DWH oil spill (EPA, 2010)**



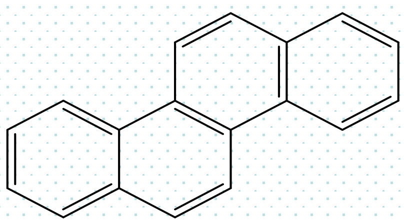
Naphthalene



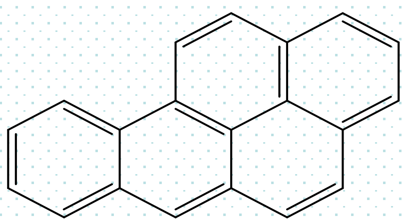
Phenanthrene



Pyrene



Chrysene



Benzo(a)pyrene

Reddy, C.M. et al. (2011) *PNAS*; EPA (2010) http://www.epa.gov/emergencies/content/ncp/product_schedume.htm

Research Objectives

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- Determine effects of oil dispersant Corexit 9500A on sorption/desorption of PAHs with Gulf Coast marine sediments
- Test effects of dispersants on desorption of aged oil from a model Gulf coast sediment

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Materials

- **Sediments**
  - ➢ **Wet sieved (75-840 μm)**
  - ➢ **Air-dried and baked at 80 ^{o}C for 6 h**
- **Seawater**
  - ➢ **0.45 μm membrane filtered**
  - ➢ **Sterilized by autoclaving**
  - ➢ **pH = 8.88, DOC = 0.43 mg/L**
- **PAHs**
  - ➢ **Naphthalene**
  - ➢ **Phenanthrene**
  - ➢ **Pyrene**
  - ➢ **^{14}C-radiolabelled**
- **Oil**
  - ➢ **Louisiana Sweet Crude Oil**

Loamy sand (SOM: 0.7%)

Sandy loam (SOM: 2.7%)

Dispersant Corexit 9500A

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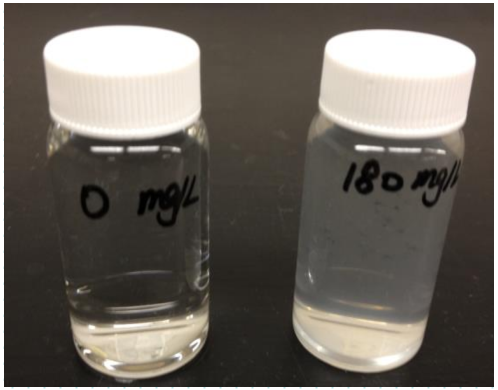
➢ Compositions

48% nonionic surfactants and 35% anionic surfactants in an aqueous hydrocarbon solvent (17%)

CAS #	Name
1338-43-8	Sorbitan, mono-(9Z)-9-octadecenoate
9005-65-6	Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs.
9005-70-3	Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs
577-11-7	Butanedioic acid, 2-sulfo-, 1,4-bis(2-ethylhexyl) ester, sodium salt (1:1)
29911-28-2	Propanol, 1-(2-butoxy-1-methylethoxy)
64742-47-8	Distillates (petroleum), hydrotreated light

Corexit 9500A



Corexit 9500A in seawater

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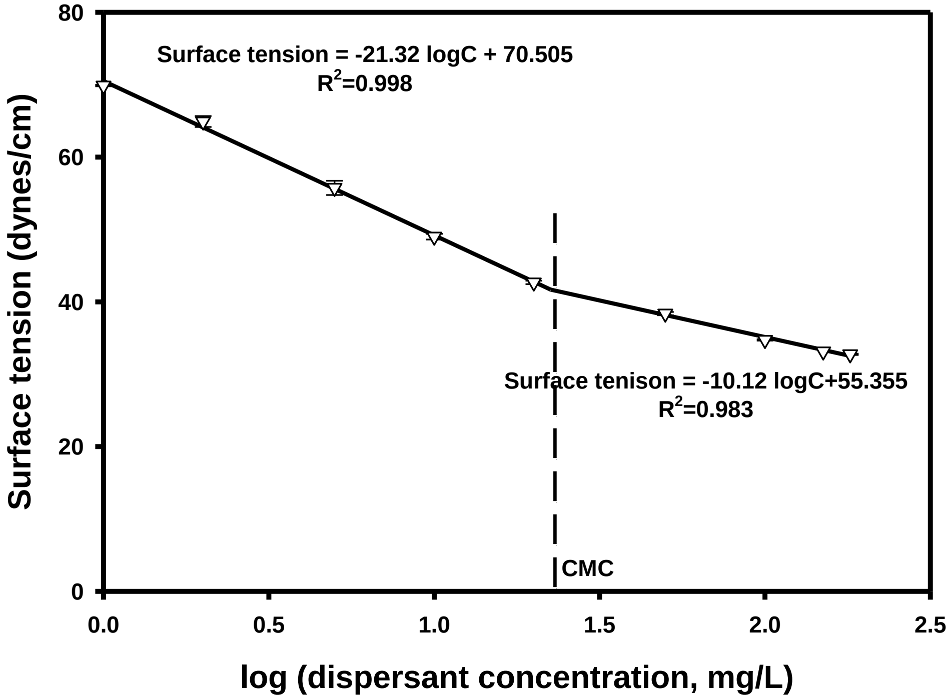
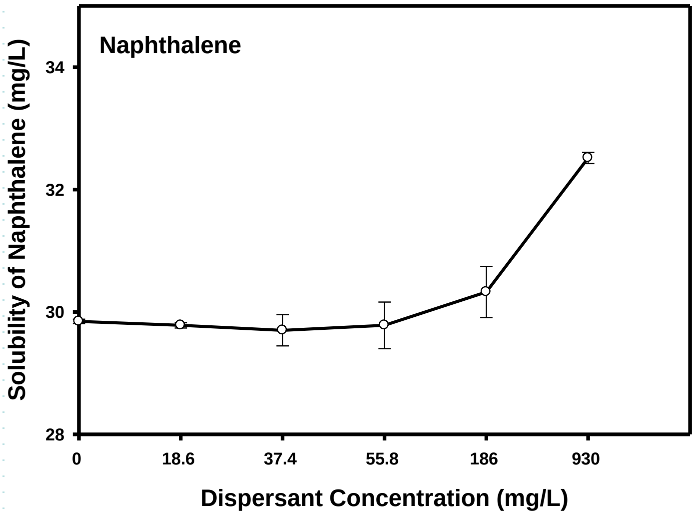
Critical Micelle Concentration (CMC) of Corexit 9500A

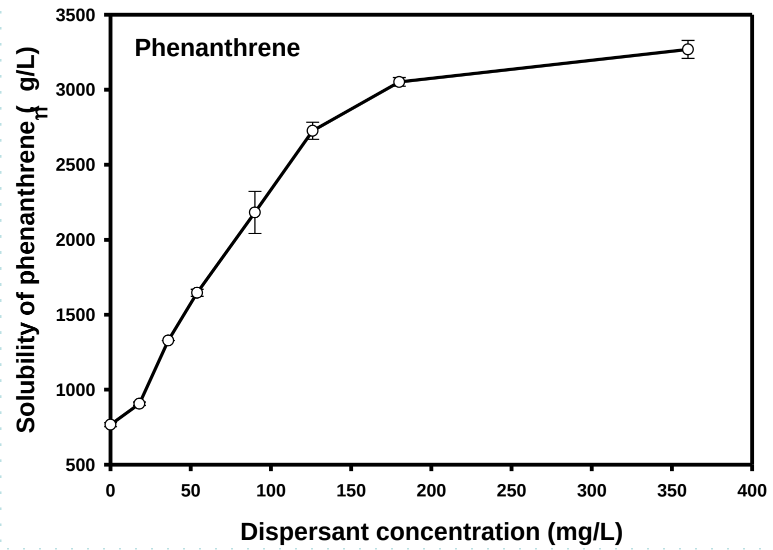


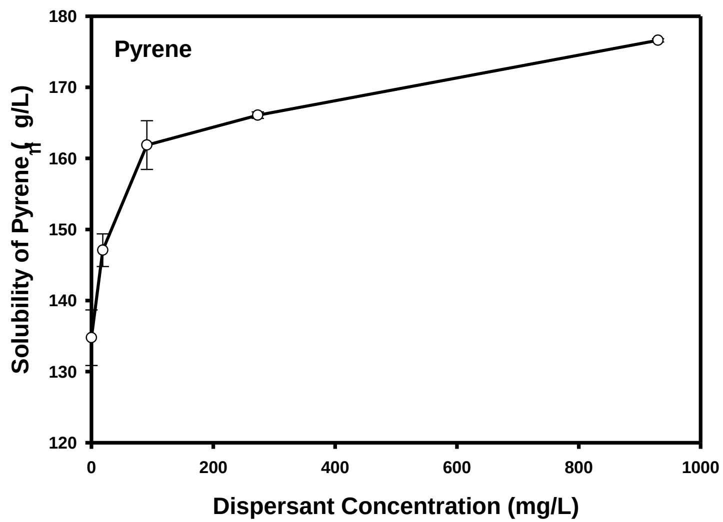
The apparent critical micelle concentration of the dispersant was determined to be 22.5 mg/L.

Gong et al. Environmental Pollution 185 (2014) 240-249
Cai et al. Marine Pollution Bulletin 109 (2016) 49–54

Dispersant Enhances PAHs Solubility

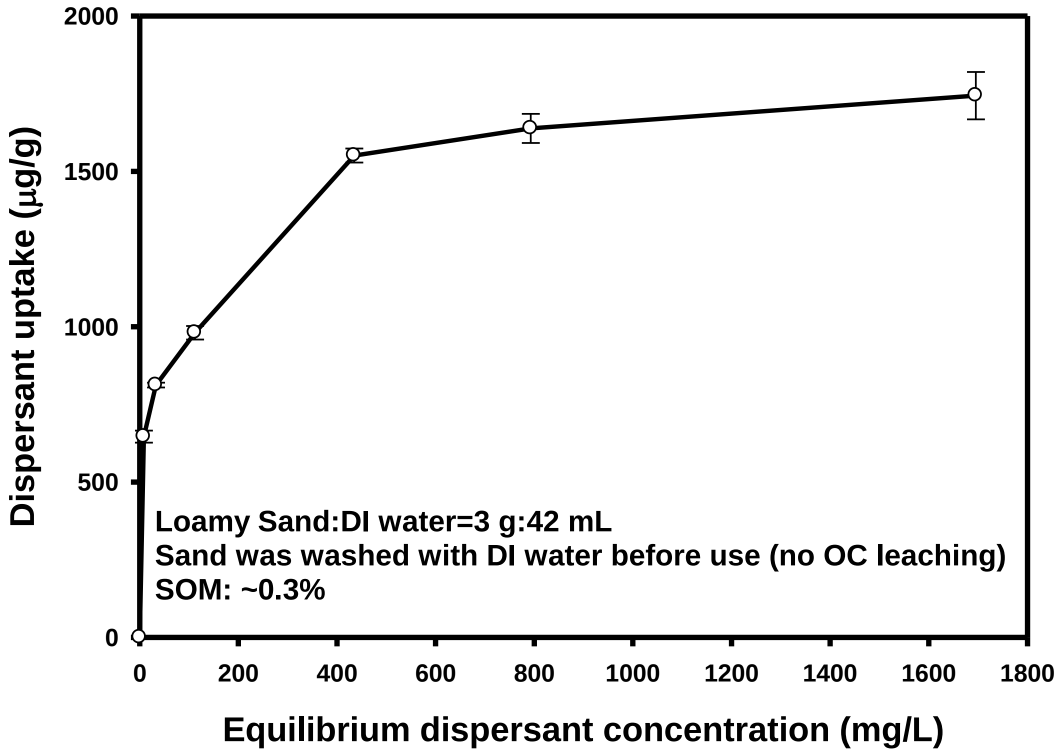






- The apparent PAH solubility in seawater increases with increasing dispersant concentration
- It is more effective for less soluble PAHs

Sorption Isotherm of Corexit 9500A on a Loamy Sand Sediment



Despite the low SOM content (~0.3%), the loamy sand sediment offers significant uptake capacity for the dispersant

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Effects of Dispersant on Sediment Uptake of PAHs

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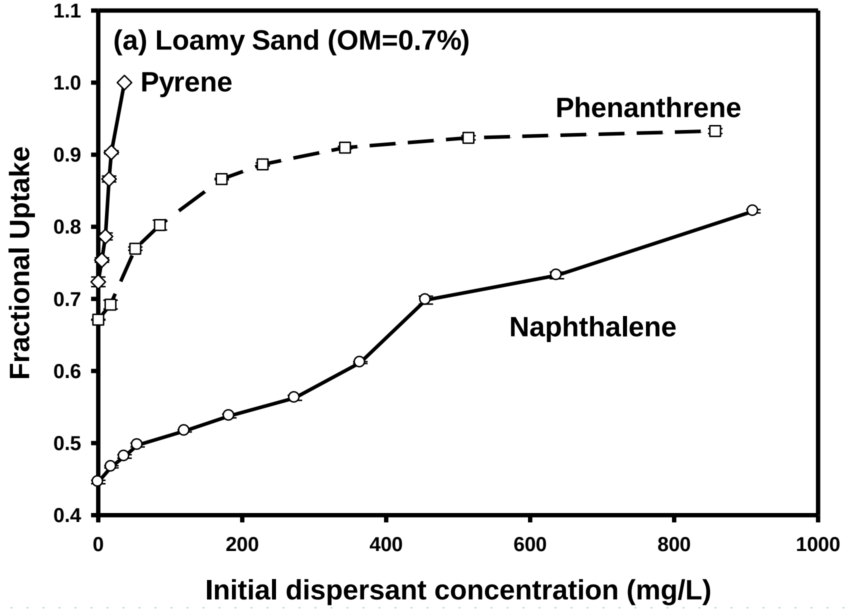

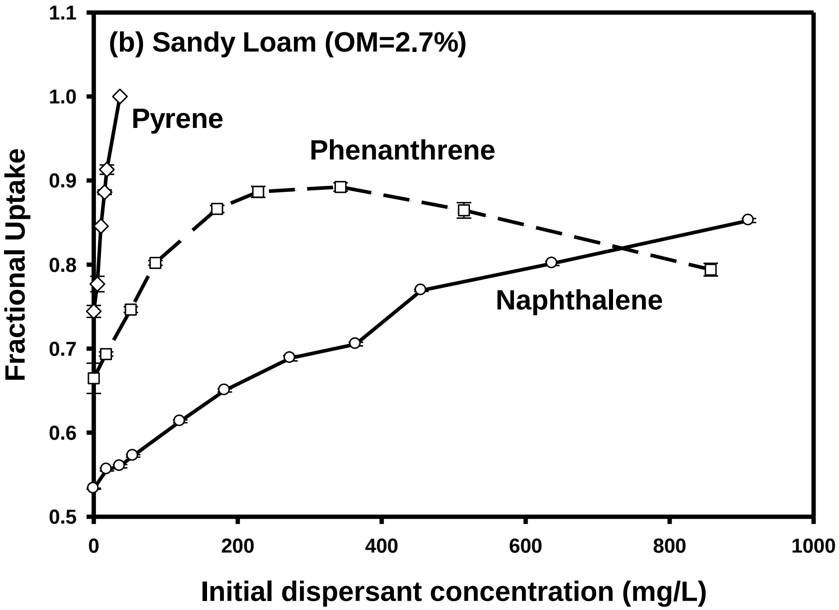

PAHs uptake increases with increasing dispersant concentration:

- ➢ Naphthalene uptake increases nearly linearly for both sediments as the dispersant increases from 0 to 860 mg/L
- ➢ Phenanthrene uptake displayed a plateau or peaking profile
- ➢ In the low dispersant range (<200 mg/L), Py>>Phen>Naph

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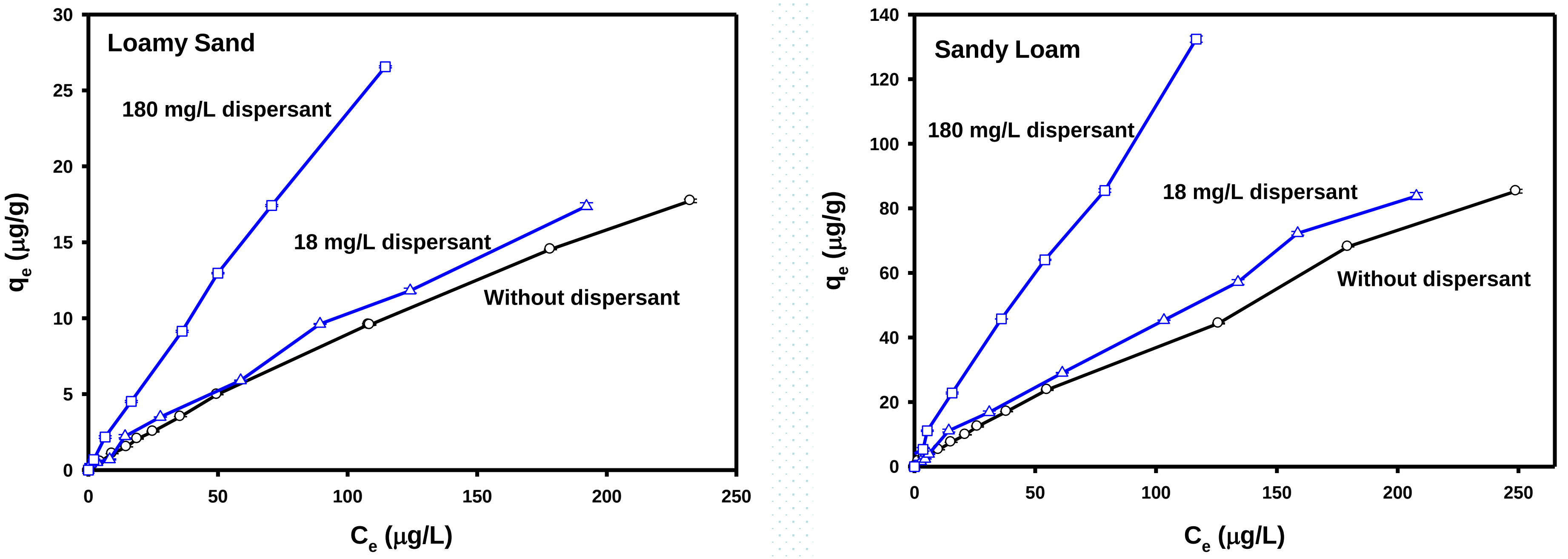
Effects of Dispersant on Phenanthrene Sorption Isotherms



(a) Increasing dispersant concentration increases phenanthrene uptake for both sediments

(b) Sediment of greater SOM shows greater dispersant effect

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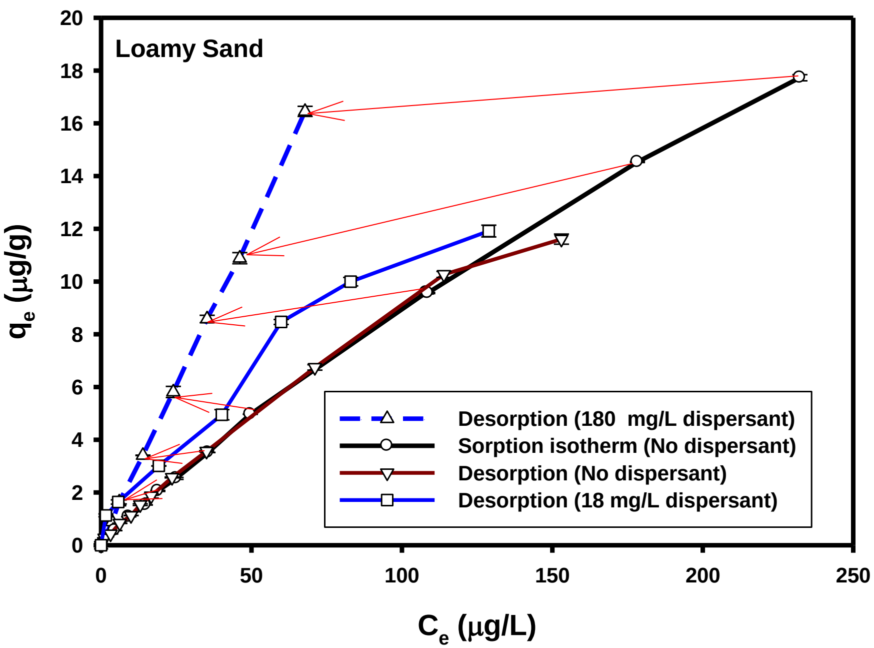
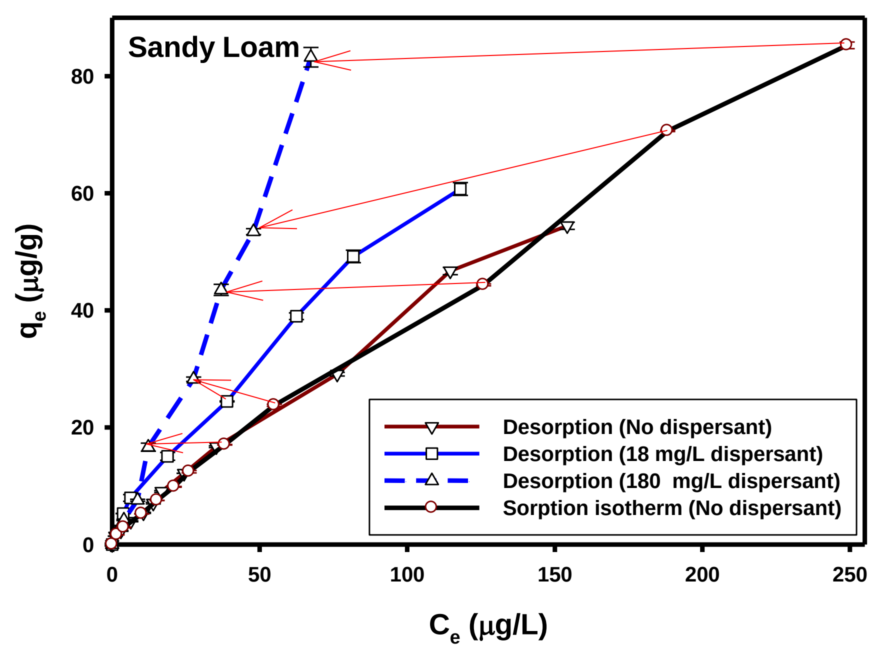
Effects of Dispersant on Desorption Isotherms and Sorption Hysteresis

Scenarios A and B

Phenanthrene pre-sorbed without dispersant, then subjected to desorption equilibrium tests with or without the dispersant





(a) Sorption is reversible without dispersant
(b) The dispersant induces a clear sorption hysteresis
(c) The extent of hysteresis increases with dispersant concentration

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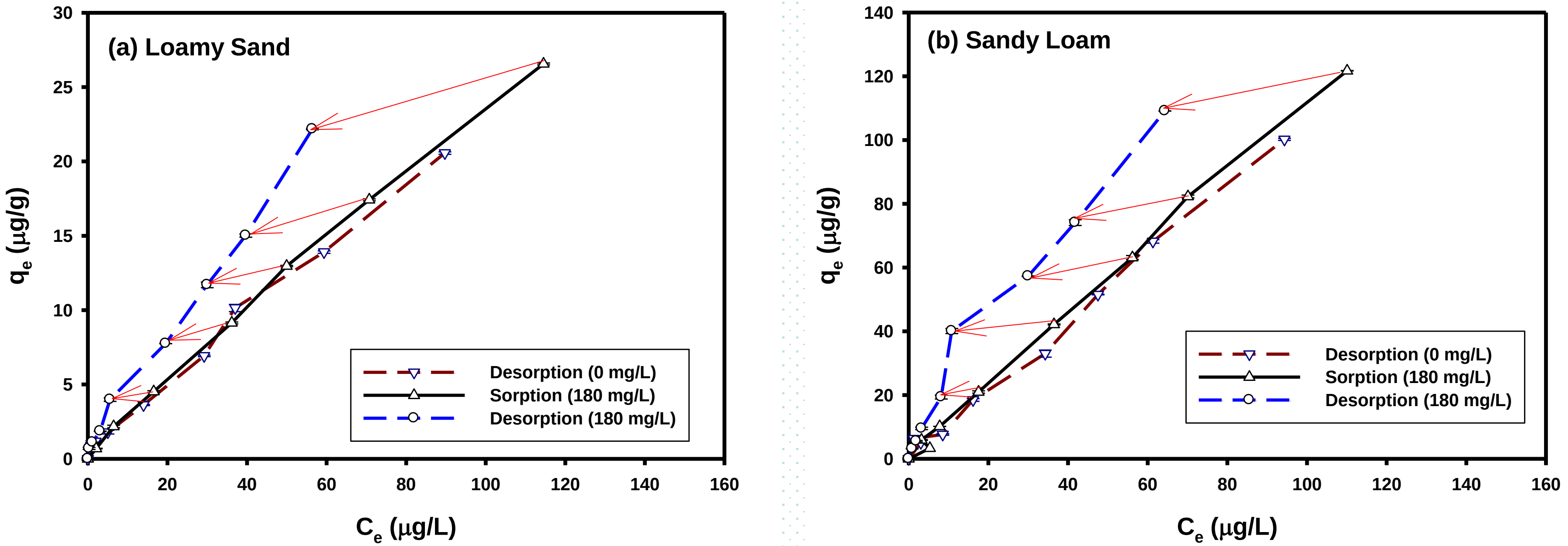
Effects of Dispersant on Desorption Isotherms and Sorption Hysteresis

➢ Scenarios C and D

Phenanthrene pre-sorbed with dispersant, then subjected to desorption equilibrium tests with or without dispersant



- **Dispersant during sorption increases capacity, but does not induce hysteresis**
- **Dispersant during desorption prompts hysteresis**

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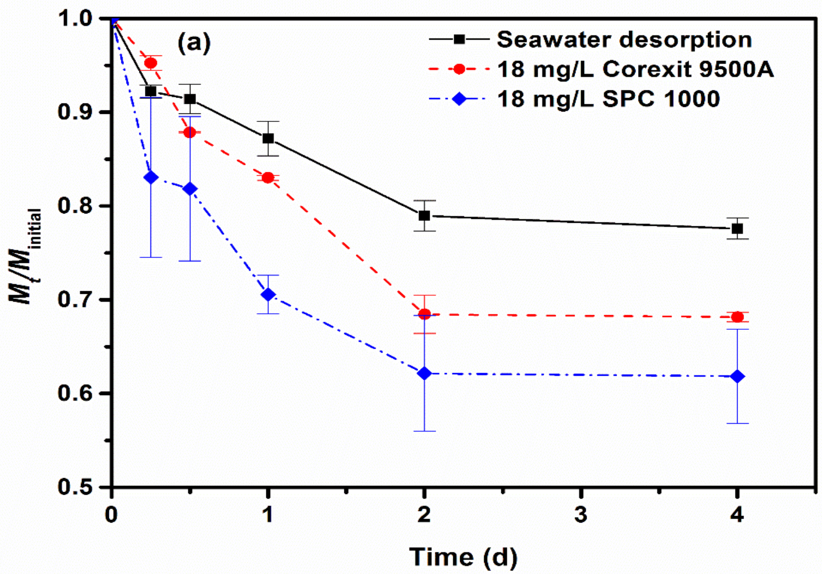
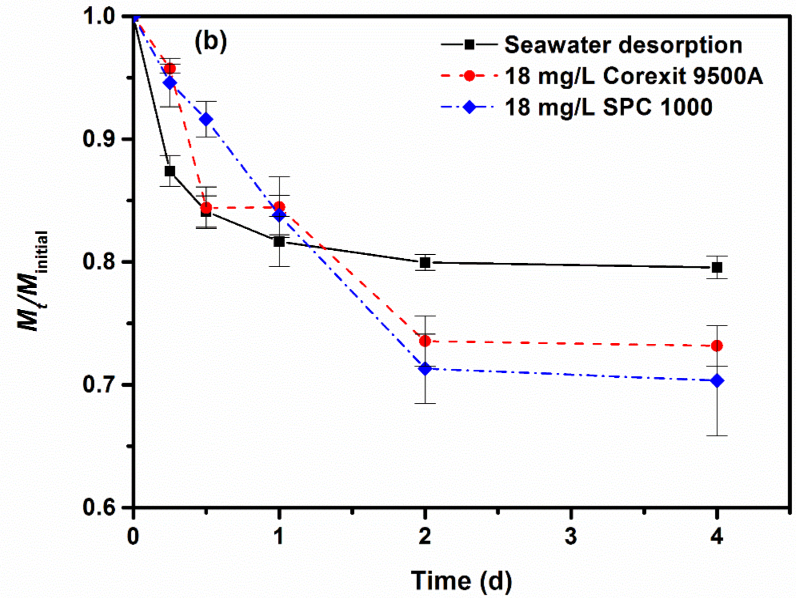
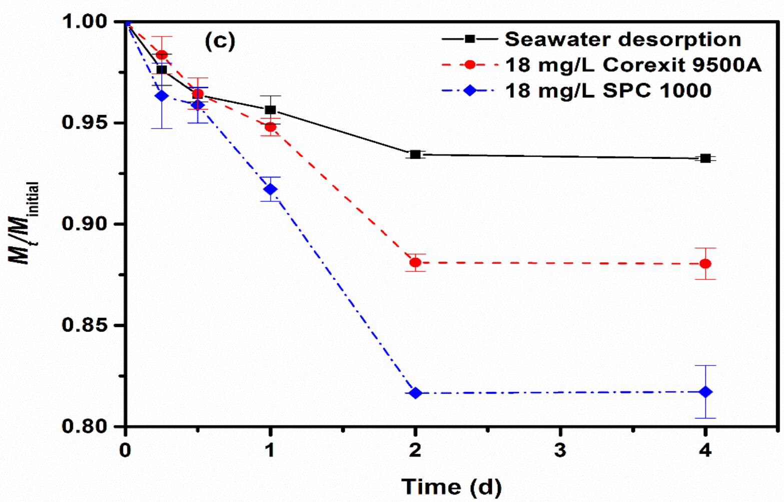
Desorption kinetics of aged DwH TPHs (a), *n*-alkanes (b) and parent PAHs (c) from Bay Jimmy sediment







- Oil was identified as the DwH oil
- pH = 7.6-8.1, salinity = 3.15%, Corexit EC9500A = 0 or 18 mg/L, SPC 1000 = 0 or 18 mg/L, and temp. = 25 ± 0.2 °C.
- M_t: mass remaining in sediment at time t, $M_{initial}$: total initial mass.
- **Both dispersants enhanced desorption, SPC being more effective**

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Part I Summary

- Dispersant Corexit 9500A enhances uptake of PAHs by marine sediments, transferring more PAHs into sediment
- Dispersant-facilitated transfer of PAHs to sediments should be taken into account in evaluating fate and transport of oil
- For newly adsorbed PAH, the presence of dispersant during desorption retards desorption of PAHs, resulting in sorption hysteresis
- For field sediment 5 years after the spill, dispersants enhance desorption of oil components
- WAO and dispersed oil increases sediment sorption of PAHs

Part II. Effects of dispersants on settling of marine sediment particles and particle-associated transport of oil components

Zhengqing Cai, Jie Fu, Wen Liu, Xiao Zhao, SE O'Reilly, and Dongye Zhao. (2017) "Effects of oil dispersants on the settling performance of marine sediment particles and transport of oil/PAHs in seawater" *Marin Pollution Bulletin*, 408-418.

Research Objectives

- Test effects of dispersants on the settling behaviors of sediment particles
- Explore how dispersant-facilitated particle sedimentation affects distribution and transport of important oil components in sediment-water systems

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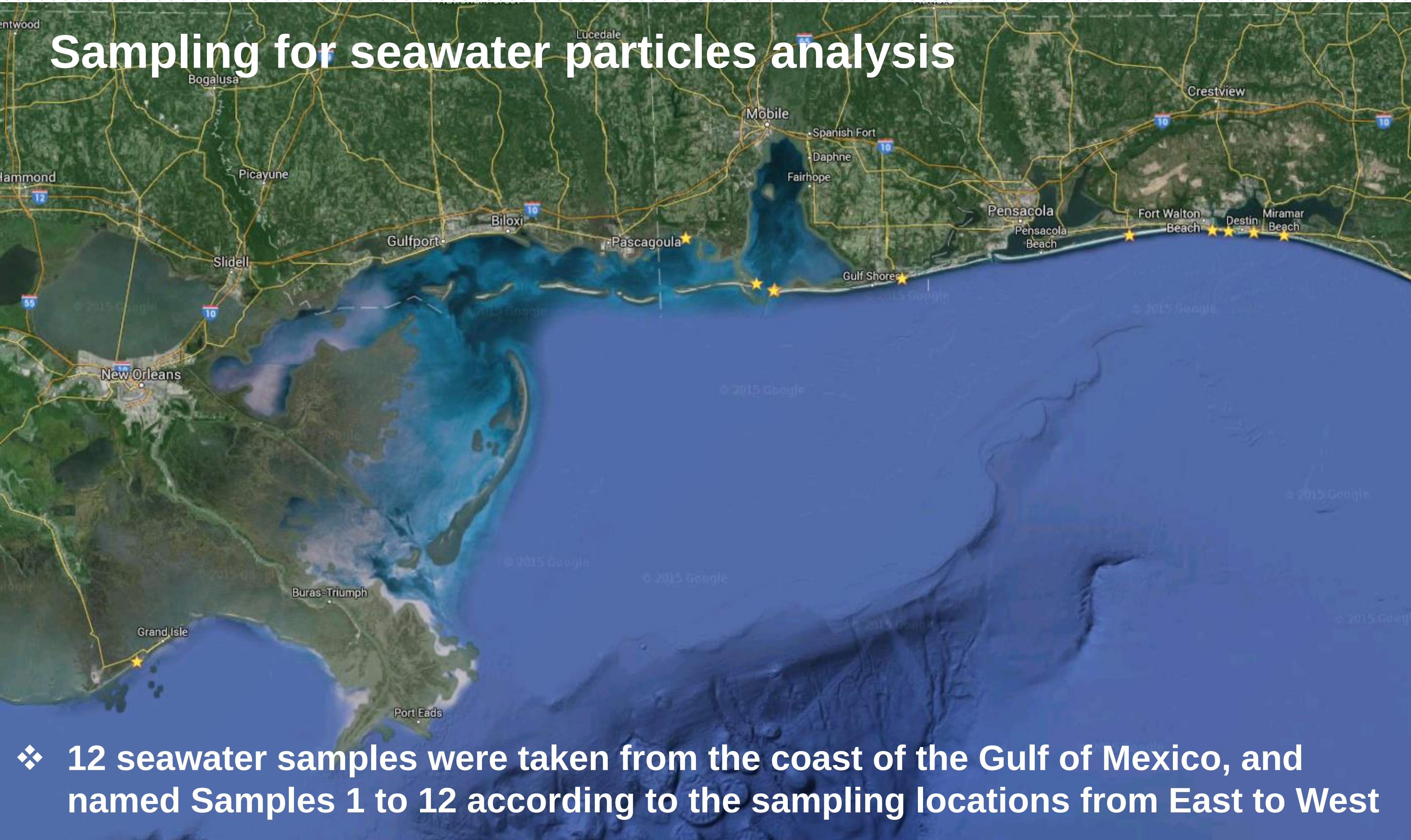
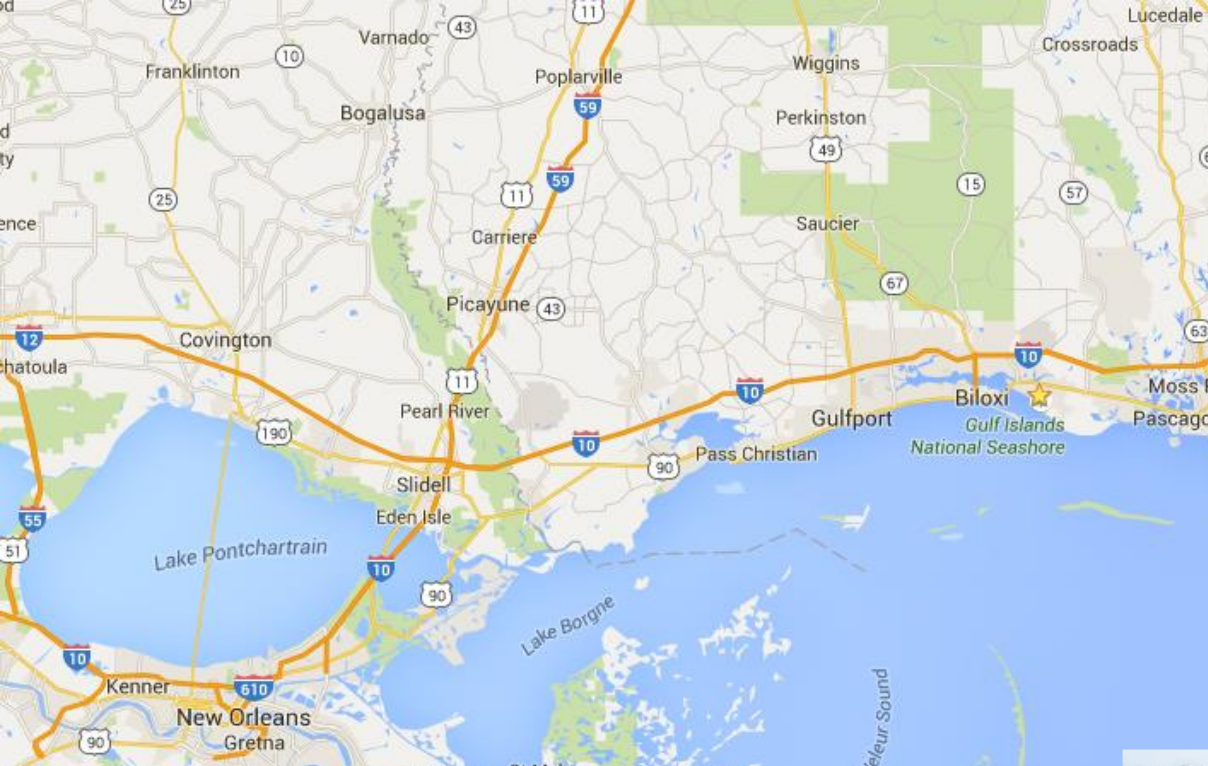
Seawater Sampling

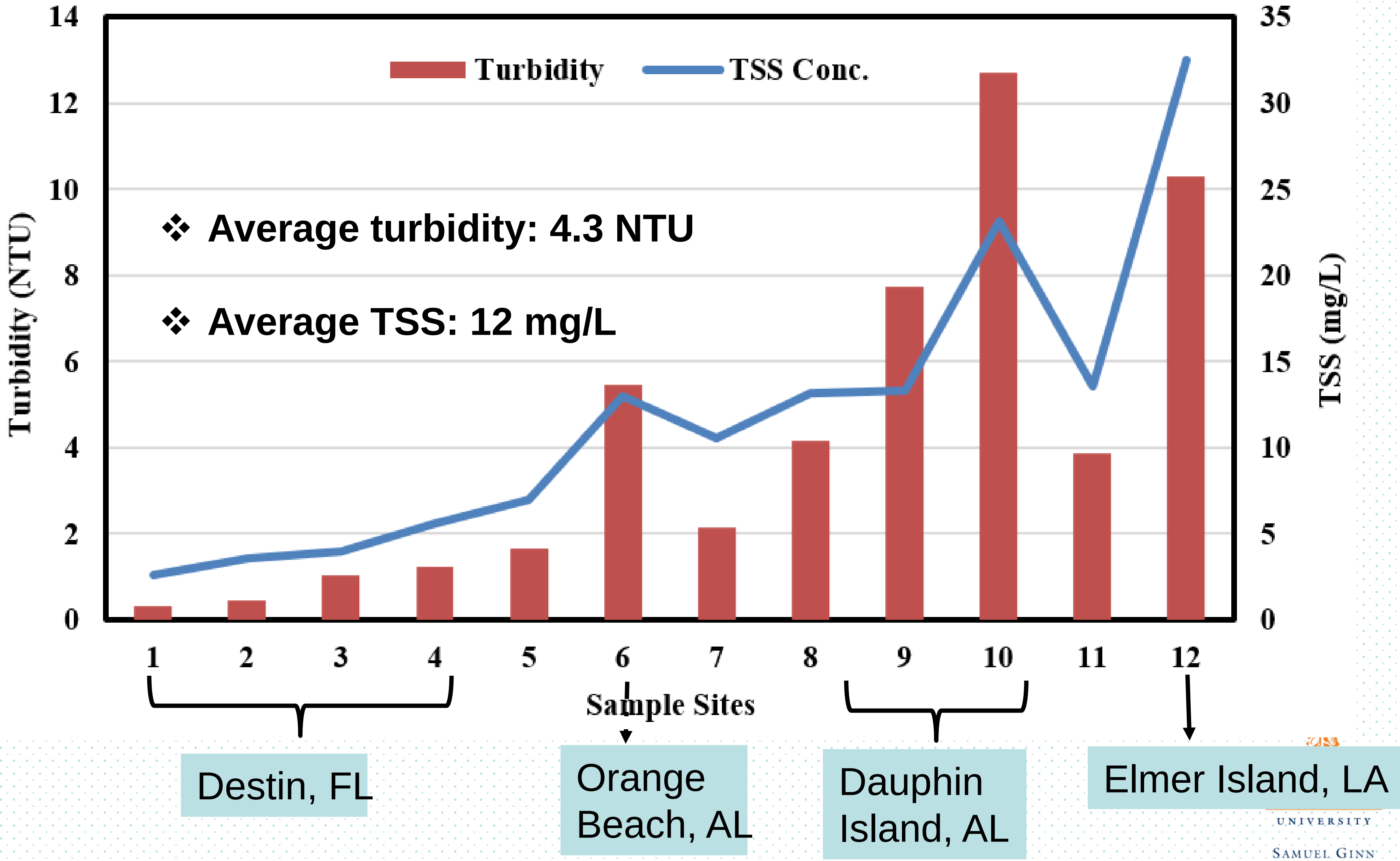
Sampling for seawater particles analysis



- 12 seawater samples were taken from the coast of the Gulf of Mexico, and named Samples 1 to 12 according to the sampling locations from East to West


Varnado
Franklinton
Poplarville
Wiggins
Lucedale
Crossroads
Bogalusa
Perkinston
Carriere
Saucier
Picayune
Covington
Pearl River
Biloxi
Gulfport
Moss P
Pascagou
Gulf Islands National Seashore
Pass Christian
Slidell
Eden Isle
Lake Pontchartrain
Lake Borgne
Kenner
New Orleans
Gretna
Breton Natio
Wildlife Refu

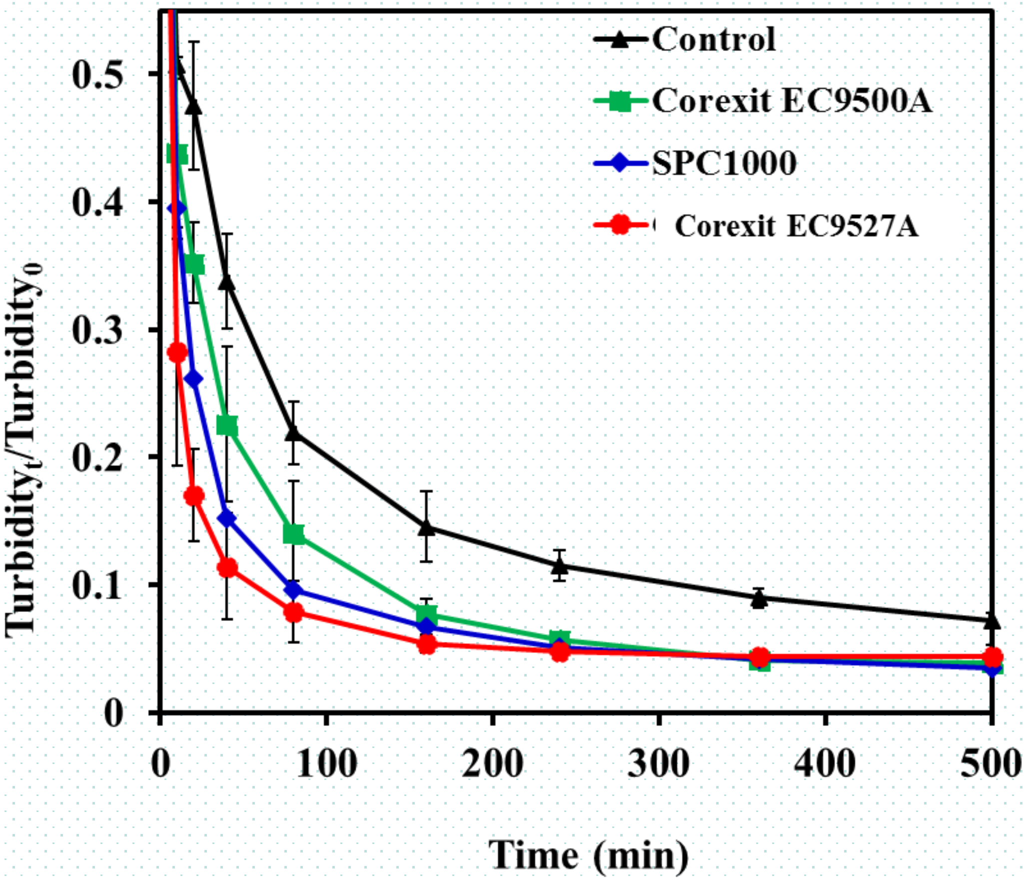
Turbidity and Concentration of Suspended Particles



Materials and Methods

- Fill 300 mL of filtered seawater in amber bottles, mixed with sediment (<0.84 mm)
- Add dispersant, mix on a shaker at 200 rpm for 12 hours and 50 rpm for 5 minutes
- Keep the bottles still, take samples for turbidity measurement at predetermined time intervals

Effects of Three Different Dispersants

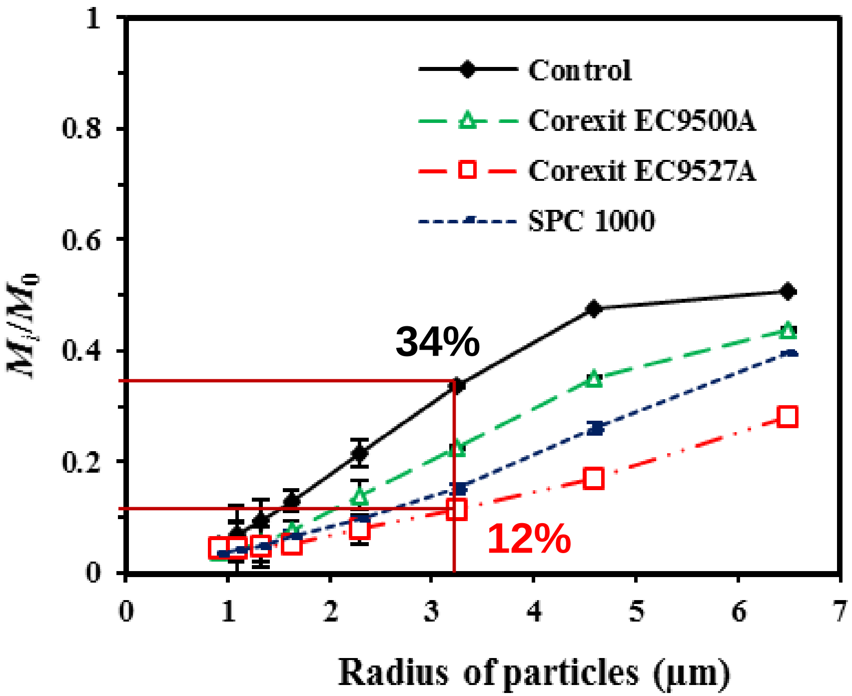


Reaction conditions:

Sediment = 12 g/L
Dispersant = 5 mg/L
Temperature = 25 ℃

- ❖ **All three dispersants accelerated the settling rate of resuspended sediment particles**
- ❖ **Corexit EC9527A is most effective**

Effects of Different Dispersants



Stokes' law:

$$V = \frac{2\,(\rho_p - \rho_f)}{9\,\mu} g R^2$$

V is the settling velocity of particle (m/s)
g is 9.8 m/s^2
ρ_p is 2069 kg/m^3
ρ_f is seawater density, 1024 kg/m^3
μ is the dynamic viscosity (9.594×10^{-4} kg/m·s)
R is the radius of the sediment particle (m)

❖ **Dispersants enhanced aggregation of the fine particles**

Mo is the total mass of all particles, and Mi refers to the mass of particles with radius less than the corresponding x-axis value.

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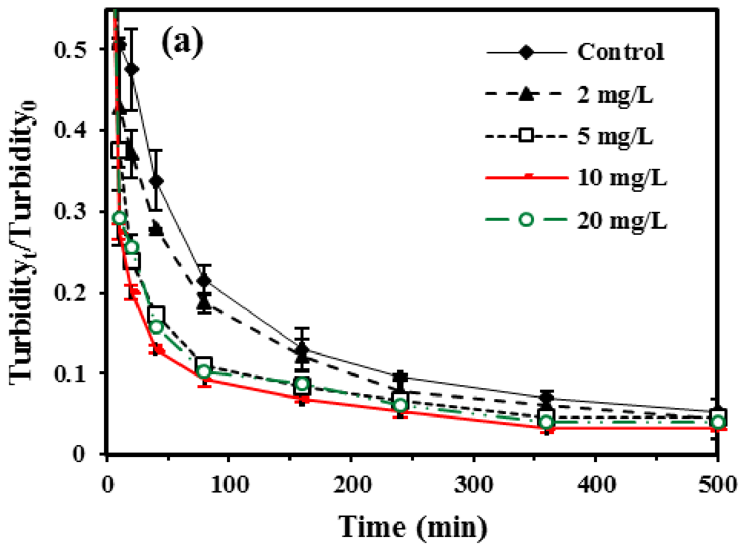
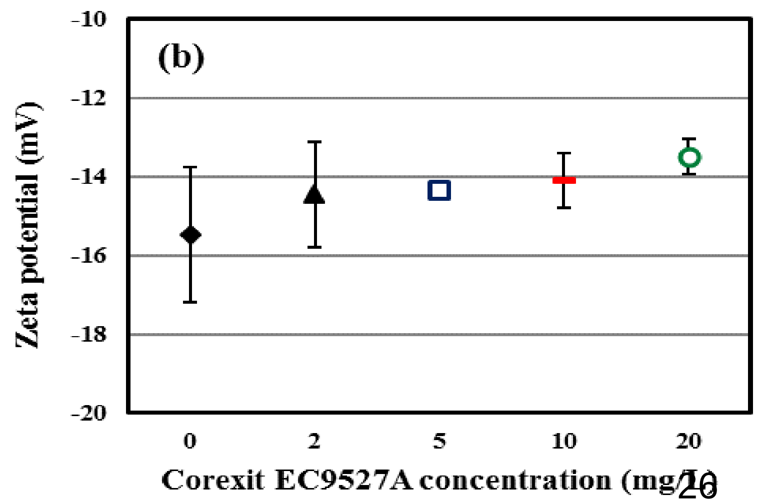
Effects of Dispersant Concentration

Experimental conditions:

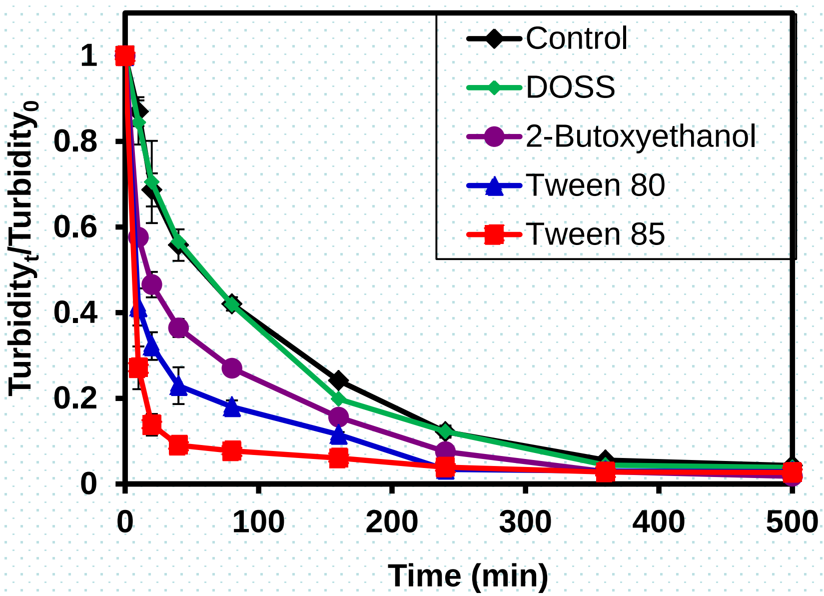
Sediment = 12 g/L
Temperature = 25 ℃
pH = 7.3 ± 0.3

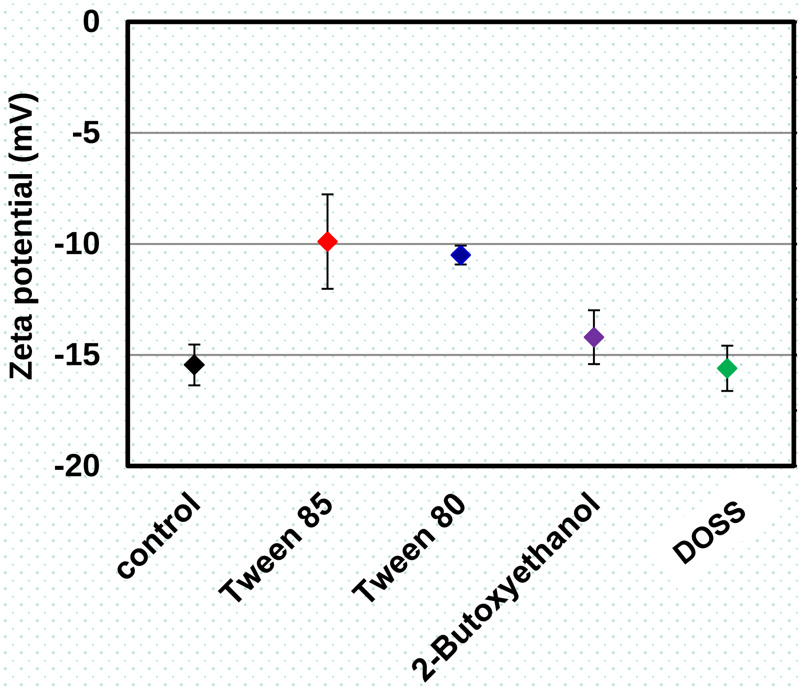


- **Increasing dispersant from 0 to 10 mg/L increases settling rate of sediment**
- **Further increasing dispersant shows insignificant additional effect**
- **Dispersant modestly suppresses the zeta-potential of particles**



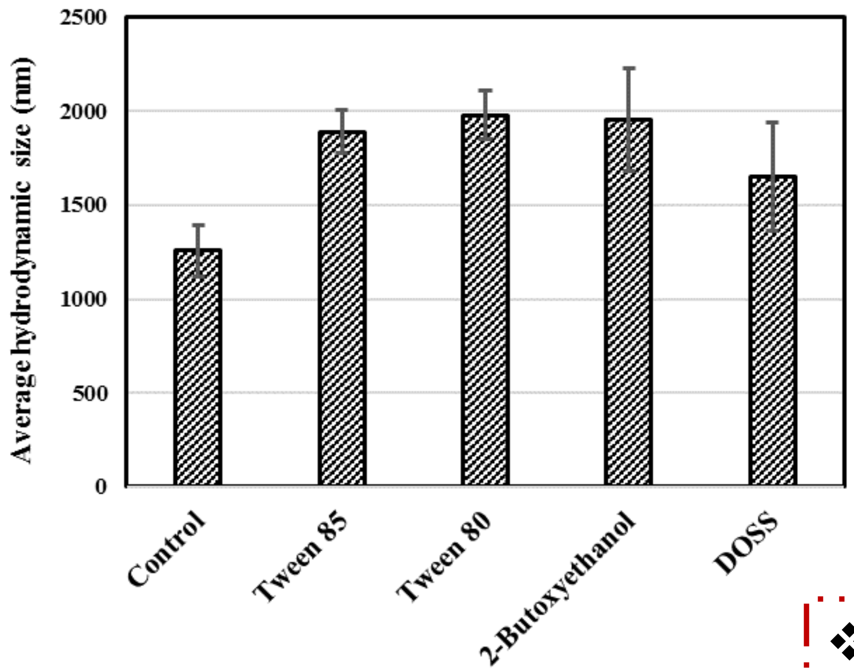
Effects of Individual Dispersant Components





- ❖ The **nonionic surfactant** components (Tween 80 and Tween 85) are most effective in enhancing the settling rate
- ❖ The organic solvent, **2-butoxyethanol**, also enhances the settling rate

Effects of Dispersants on Hydrodynamic Particle Size



Experimental conditions:

Temperature = 25 ℃
Dispersant components conc. = 10 mg/L
pH = 7.3 ± 0.3

The sediment with size <10 μm were obtained by taking the supernatant after 80 min gravity settling
The hydrodynamic size was monitored using the Malvern Zetasizer

- **Tween 80, Tween 85 and 2-butoxyethanol increased the hydrodynamic particle size of suspended particles/aggregates**

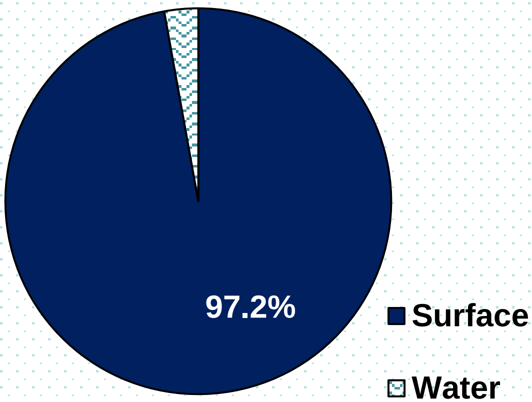
Equilibrium Distribution of Oil Between Sediment and Seawater

- **Fill 300 mL seawater in amber bottle, mixed with sediment**
- **Add crude oil and dispersant (ratio = 20:1), mix on shaker for 12 hours**
- **Keep the bottles still for 12 hours to allow different phases to separate**
- **Extract oil in each phase by dichloromethane and analyzed by GC-MS and GC-FID**

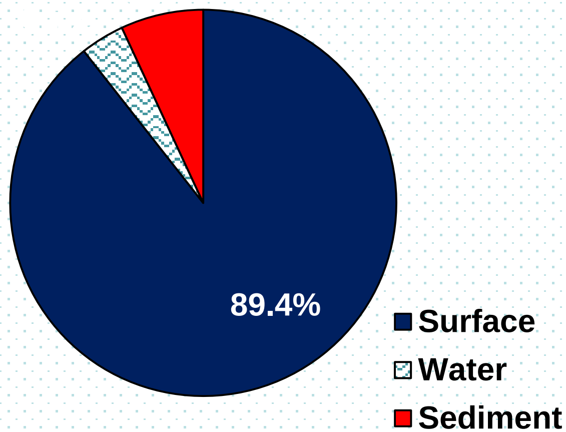
Agilent GC-MS

Distribution of TPHs in Various Systems

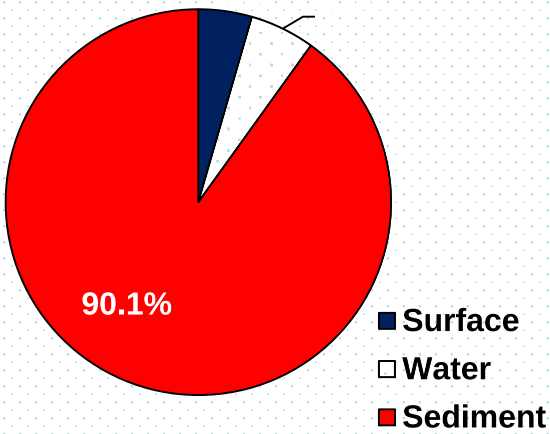
1. Oil & water



2. Oil & water & sediment



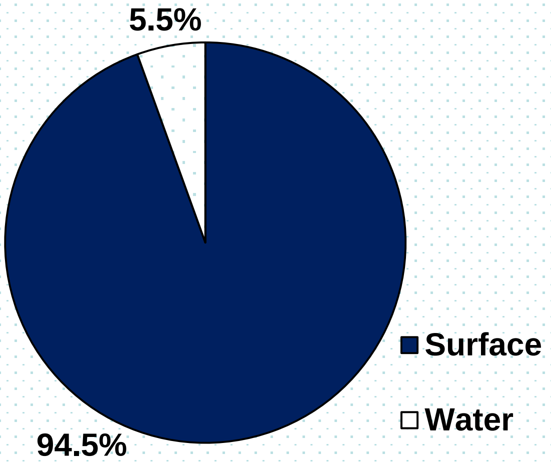
3. Oil & water & sediment & dispersant



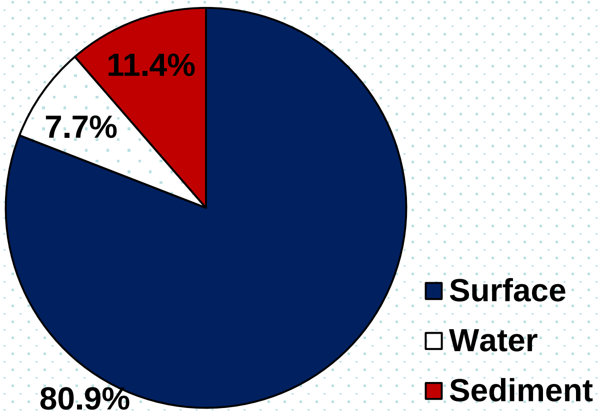
- **The presence of dispersant increases oil in water phase, but when sediment is present, the dispersant will facilitate transferring much more surface oil into the sediment phase (from 6.9% to 90.1%)**

PAHs distribution

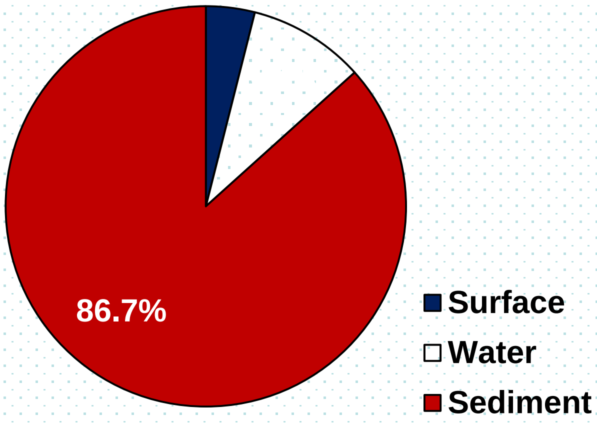
1. Oil & water



2. Oil & water & sediment

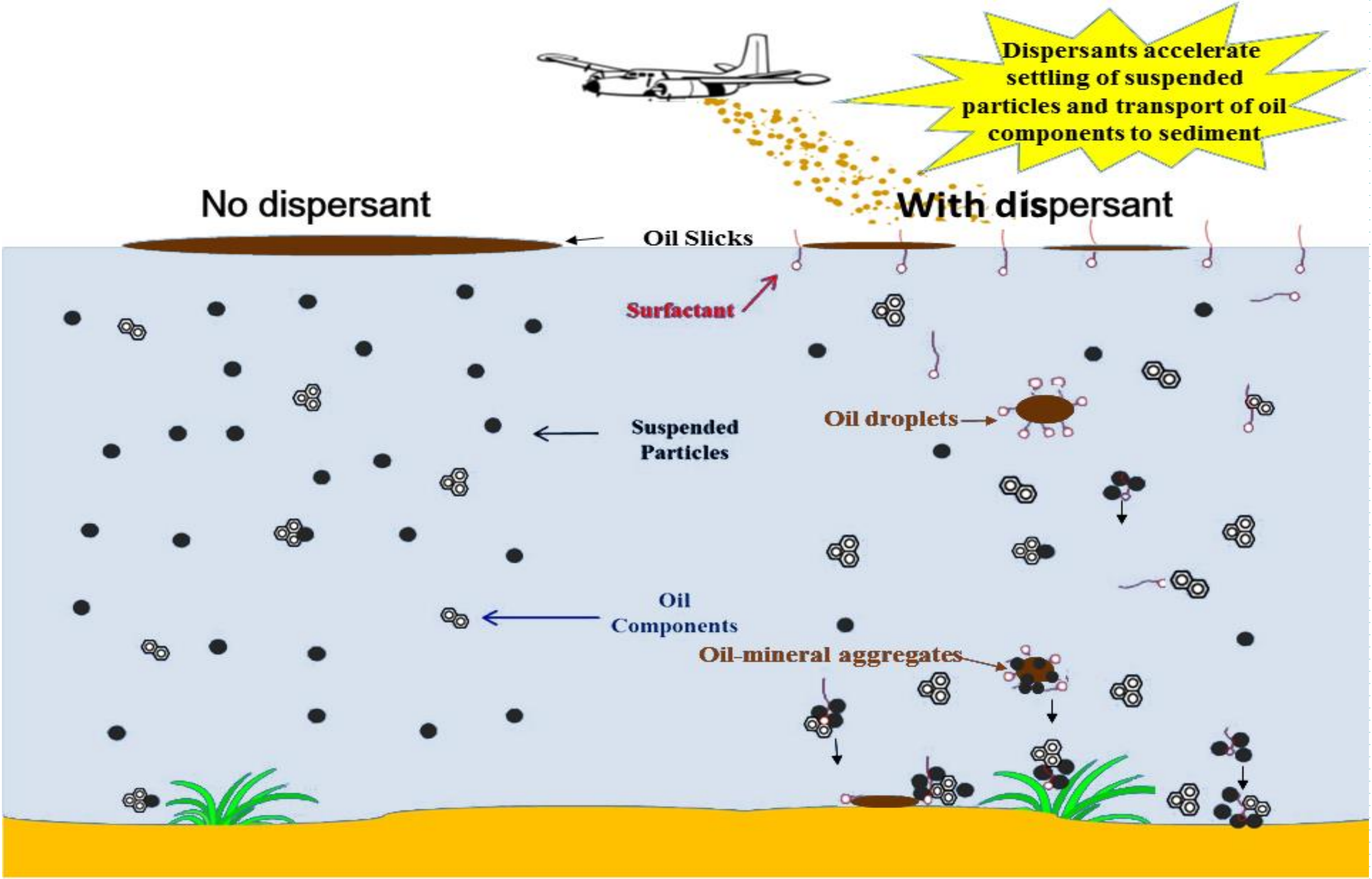


3. Oil & water & sediment & dispersant



❖ Dispersant increases PAHs in the water phase, and increases the transport of surface PAHs to the sediment phase (from 11.4% to 86.7% in the sediment phase)

Effect of dispersant on oil transport



Part II Summary

1. All three model dispersants accelerated the settling rate of suspended sediment particles
2. Tween 80 and Tween 85 are the most effective components for enhancing aggregation of sediment particles
3. Oil dispersants increased the formation of oil-mineral aggregates and facilitated transferring of oil slicks to the sediment phase
4. A low-cost effective rapid response technique may be conceived by treating spilled oil with oil dispersants along with proper sediment particles

Part III. Effects of Oil and Dispersant on Formation of Marine Oil Snow and Transport of Oil Hydrocarbons

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[a] Department of the Interior, Gulf of Mexico OCS

Office of Environment, New Orleans, LA

J. Fu, Y. Gong, X. Zhao, S. E. O'Reilly, D. Zhao (2014) *Environmental Science & Technology,* 48: 14392−14399.

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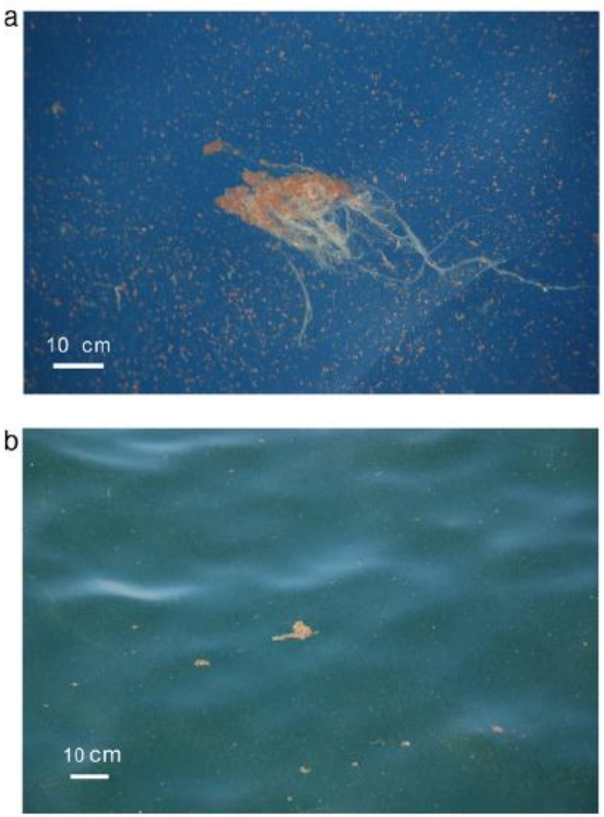
Formation of Marine Snow

- ✓ **Organic and inorganic particles or aggregates (≥0.5 mm)**
- ✓ **Naturally formed in the ocean, consisting of minerals, detritus, bacteria mucus, phytoplankton, and zooplankton feces**
- ✓ **Physico-chemical processes (e.g., wave action, coagulation/ flocculation) and microbial actions are involved**



From Passow, et al

Shortly after the DwH spill, marine oil snow (MOS) of very large size (>1 cm) was observed (*Passow et al. 2012*)

Passow, U., Ziervogel, K., Asper, V., & Diercks, A. (2012).. *Environmental Research Letters*, *7*(3), 035301.

Research Questions and Objectives

- **How oil and oil dispersants affect formation of MOS?**
- **What are the roles of microbial activities in MOS formation?**
- **How MOS affects transport of oil components?**

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Research Approach

Roller table experiments (GoM seawater)

Under Simulated hydrodynamic conditions

MOS

Factors affecting MS Formation:

Oil

Dispersant

Natural suspended solids

Indigenous microorganisms

Characterization

Particle number (*N*)

Mean diameter (D_m)

Total volume (TV)

Mean sinking/rising velocity (V_{ms}/V_{mf})

Formation mechanisms

Distribution of n-alkanes in seawater and MOS phase

Influence of MOS on fate and transport of oil hydrocarbons

Materials and Methods

- ✓ **Seawater: from Grand Bay, AL, USA**
- ✓ **Oil: Surrogate Louisiana Sweet Crude oil (*BP*) (0.06%, v/v)**
- ✓ **Dispersant: Corexit EC9500A (0.003% v/v)**
- ✓ **Roller table operated for 28 days with 250 mL round glass bottles under VII scenarios**

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Marine Snow Formation under Various Scenarios

Case	Formation of marine snow	Aggregates type	Maximum mean diameter
I: Seawater only	No	/	0.48 mm (day 25)
II: Seawater + oil	Yes (day 2)	Flocs, strips (day 6)	2.10 mm (day 6)
III: Seawater + dispersant	Yes (day 1)	Flocs	1.65 mm (day 3)
IV: Seawater + oil/dispersant	Yes (day 2)	Flocs	1.55 mm (day 4)
V: Filtered seawater + oil	No	/	/
VI: Sterilized seawater	No	/	0.34 mm (day 26)
VII: Sterilized seawater + oil	No	/	0.39 mm (day 12)

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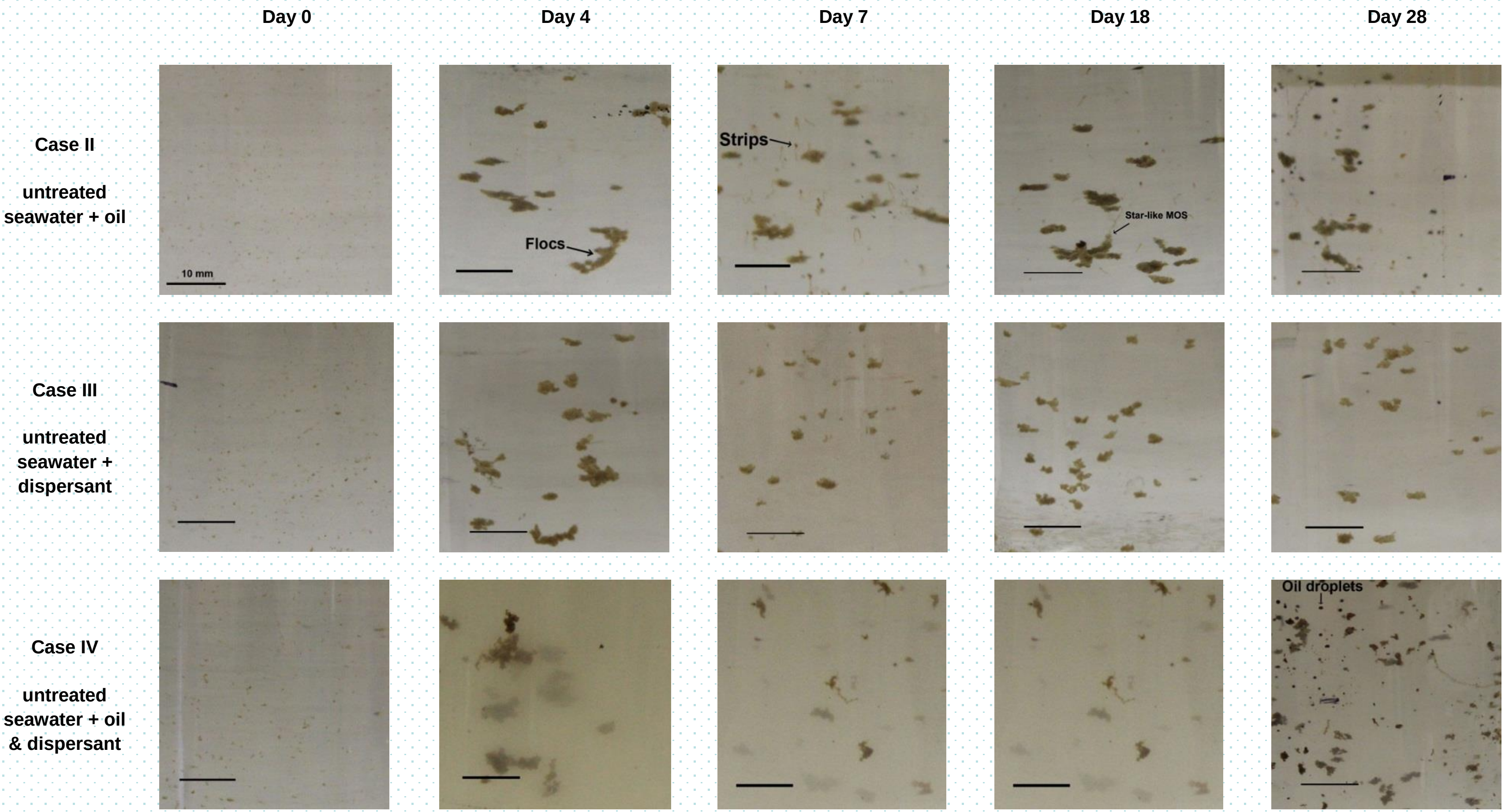
Formation of MOS in Cases II, III and IV



Remarks: **1) The changes in size, shape, number and density reflect the dynamic nature of MOS and bacterial activities; 2) The flocculation appears reversible**

Marine Snow Formation under Various Scenarios

- ✓ **Without oil or dispersant (Case I), the particles aggregated slowly and no MS was formed during the incubation time**
- ✓ **Suspended particulate matter (SPM) is required for MS formation (Case V)**
- ✓ **Active indigenous microorganisms play critical roles in MS formation (Cases VI and VII)**
- ✓ **The presence of oil (Case II), dispersant (Case III) or a combination of both (Case IV) greatly promotes the aggregation of SPM and formation of large MS flocs**
- ✓ **Without oil, all MS flocs sink (Case III), while the presence of oil or oil+dispersant renders part of MOS flocs to float**

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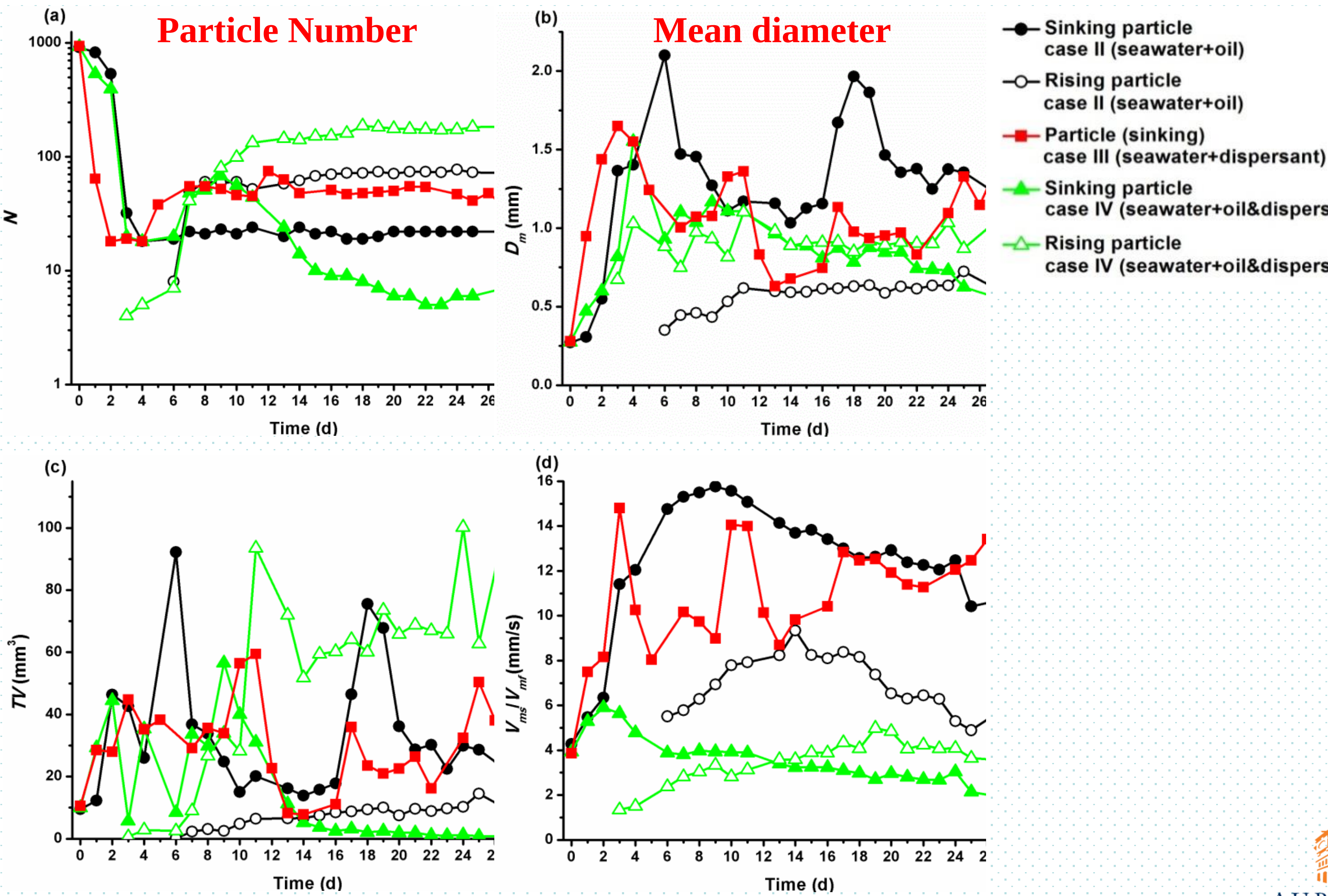
Formation of MOS: Particle Characteristics



Total volume

Mean sinking and rising velocity

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Formation of MOS: Characteristics

✓ **Compared with Cases II (oil only) and III (dispersant only), the flocs in Case IV (oil + dispersant) are more abundant in number, larger in volume, but smaller in size**

✓ **The dispersant breaks oil slicks into smaller oil droplets, preventing formation of large MOS flocs**

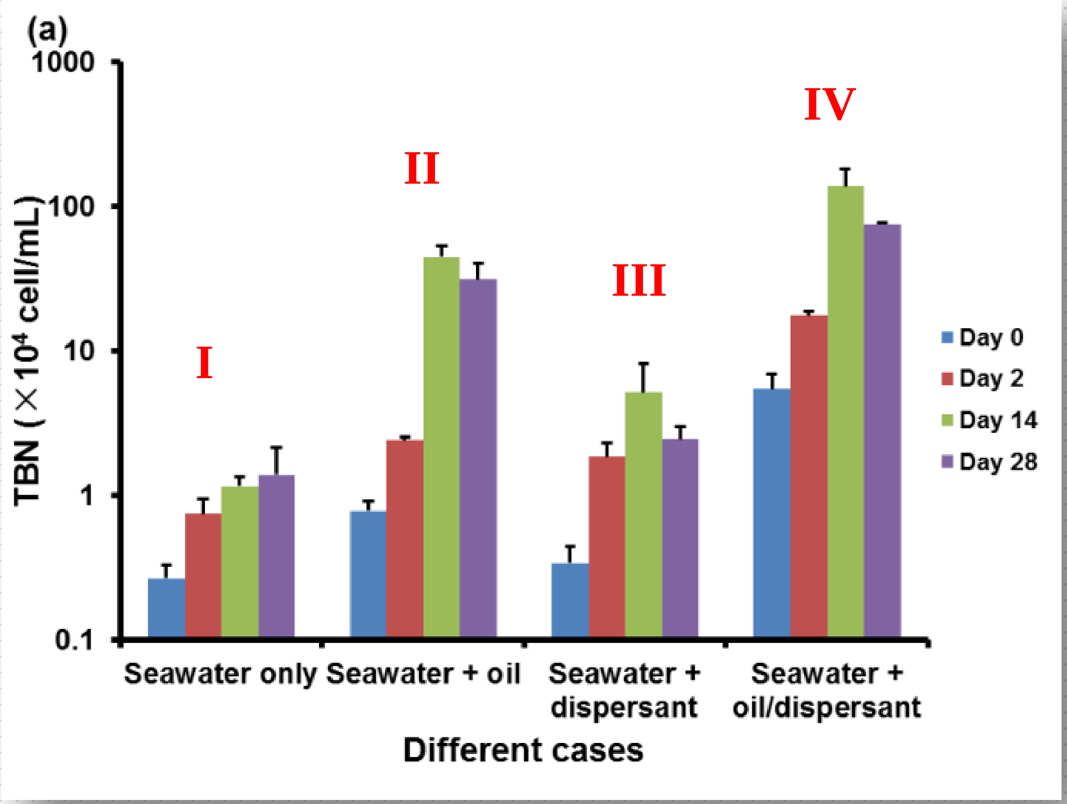
✓ **The particle sinking velocity in Case II and III is ~15 mm/s, compared to ~ 6 mm/s for Case IV**

✓ **The particle rising velocity in Case II is ~9 mm/s, compared to ~5 mm/s for Case IV**

✓ **The presence of oil causes some MOS to float, indicating incorporation light oil components in MOS**

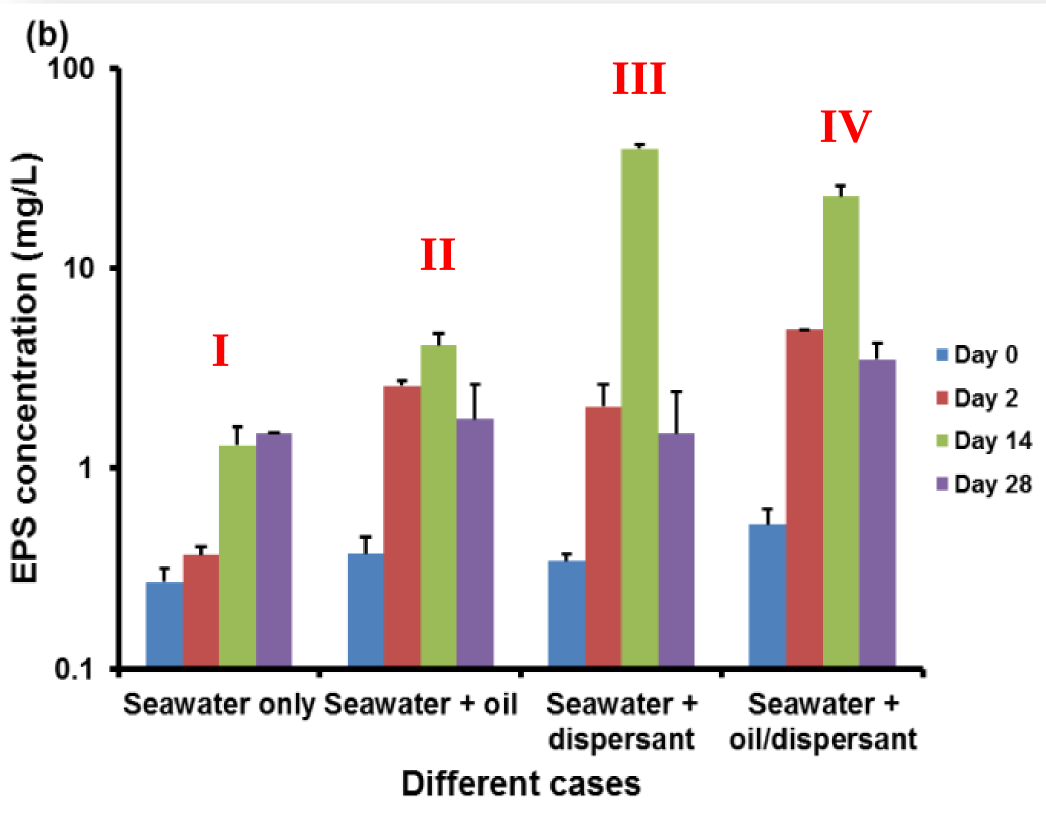
✓ **Most MOS tends to float in Case IV (oil + dispersant)**

Formation of MOS: Change of Total Bacterial Count (TBN)



- ✓Case I (seawater only): TBN gradually increased and the initial TBN was lower than that with oil
- ✓Cases II and IV, the oil associated microbes thrived from Day 0 to Day 14, but slightly declined on Day 28
- ✓ While both oil and dispersant promoted the bacterial growth, oil or dispersed oil had a greater effect on TBN

Formation of MOS: Change of Extracellular Polymeric Substances (EPS) Content



✓Case I (seawater only): EPS increased slowly and to a lower level

✓Cases II-IV: similar to the patterns of TBN, EPS rapidly increased in the first stage (0-14 days), then underwent a sharp fall on Day 28, indicating severe endogenous decay of EPS in the late incubation phase

✓While oil promoted TBN more than the dispersant, the dispersant impacted EPS more than oil. On Day 14, EPS in Cases II-IV increased by 11, 115 and 44 folds, while only 5 folds for Case I

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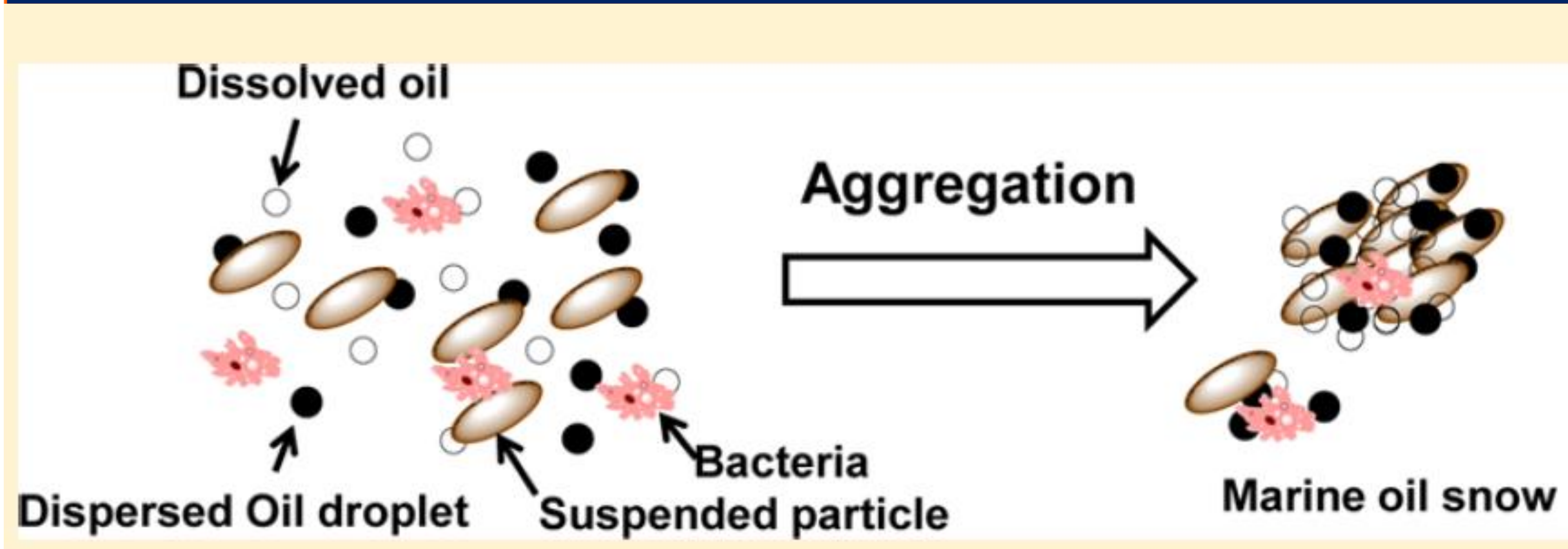
MOS Formation Mechanisms



✓ SPMs including active microorganisms are needed for MS formation

✓ Both DLVO and non-DLVO (e.g., hydrophobic forces) interactions are operative in the particle aggregation and flocculation processes. The breakup of initially formed large MS/MOS flocs suggested that the flocculation was at least partially reversible (i.e., the secondary minimum is important in MS formation)

MOS Formation Mechanisms

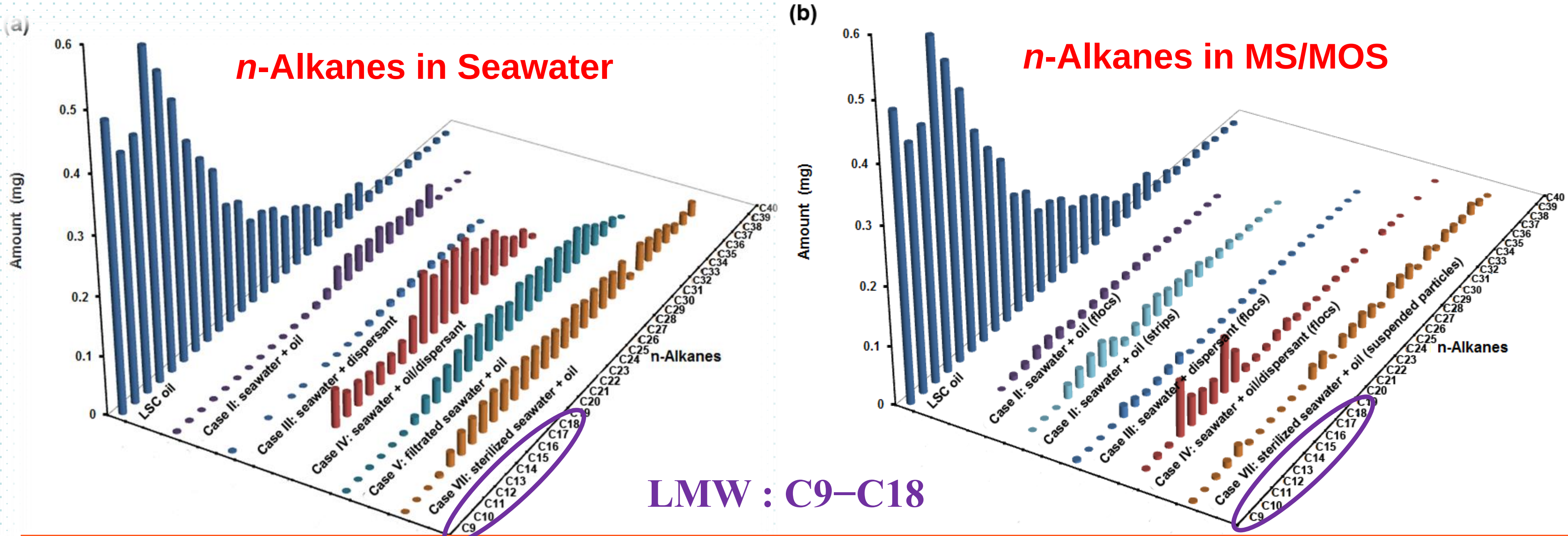
Oil and dispersant: **(1) Dispersed oil reduces the repulsive energy and promotes particle aggregation by lowering zeta potential; and (2) Incorporation of dispersed oil enhances hydrophobic interactions between SPMs.**

Marine oil snow

Oil: **(1) Oil hydrocarbons enhance bacteria growth (TBN); and (2) Bio-surfactants produced by bacteria can emulsify oil and enhance biodegradation of oil hydrocarbons, which enhances interactions between hydrocarbons, bacteria and suspended particles.**

Dispersant: **(1) Lowers zeta potential, and (2) Enhances production of sticky matters (EPS) to be incorporated in SPMs and form mucus matrices.**

Mass distribution of n-alkanes (C9−C40) in seawater and in MS/MOS after 28-day roller table experiments



- ✓ ***n*-Alkanes in Seawater:** **The addition of dispersant (Case IV) increased the dissolution of *n*-alkanes than in Case I (oil only)**
- ✓ ***n*-alkanes in MS/MOS:** **Case IV showed the highest uptake (mostly low or medium MW *n*-alkanes) – dispersant facilitates both dissolution and sorption**
- ✓ **Dispersed oil resulted in smaller MOS flocs with slower sinking/rising velocities, giving a longer residence time in the water column, favoring biodegradation**

Part III Summary

1. **Both oil and the dispersant greatly promote formation of MS/MOS, and MOS flocs of 1.6−2.1 mm are developed within 3−6 days**
2. **The presence of oil + dispersant results in more and smaller MOS flocs than oil or dispersant alone; and most MOS flocs with dispersed oil tend to float**
3. **Oil enhances MOS formation by promoting the bacterial growth and enhancing hydrophobic interactions, whereas the dispersant promotes MS formation by lowering zeta potential and increasing EPS production**
4. **Natural suspended solids and indigenous microorganisms play critical roles in the MS/MOS formation**
5. **Dispersant selectively disperses *n*-alkanes (C9−C40) in seawater, and facilitates sorption of more oil hydrocarbons in MOS**
6. **More lower-molecular-weight (LMW) *n*-alkanes (C9−C18) are partitioned in MOS than in seawater in the presence of the dispersant**

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