Thank you for signing in early

The webinar will begin promptly at
12:00 pm ET, 9:00 am PT

SERDP and ESTCP Webinar Series

- The webinar will begin promptly at 12:00 pm ET, 9:00 am PT
- Options for accessing the webinar audio
  - Listen to the broadcast audio if your computer is equipped with speakers
  - Call into the conference line
    - (669) 900-6833 or (929) 205-6099
    - Required webinar ID: 405-388-708
  - YouTube live stream
    - https://www.youtube.com/user/SERDPESTCP
- For questions or technical issues, please email serdp-estcp@noblis.org or call 571-372-6565

Waste Reduction and Treatment in Armed Forces Vessel Environments

June 4, 2020

SERDP DOD • EPA • DOE | ESTCP

Welcome and Introductions

Rula A. Deeb, Ph.D.
Webinar Coordinator

Webinar Agenda

- **Webinar Logistics** (5 minutes)
  Dr. Rula Deeb, Geosyntec Consultants
- **Overview of SERDP and ESTCP** (5 minutes)
  Dr. Robin Nissan, SERDP and ESTCP
- **Characterizing Shipboard Bilgewater Emulsions Using Macro- and Micro-Scale Flows** (25 minutes + Q&A)
  Dr. Cari Dutcher, University of Minnesota
- **Emulsion Characterization Study for Improved Bilgewater Treatment and Management** (25 minutes + Q&A)
  Ms. Danielle Paynter, Naval Surface Warfare Center
- **Final Q&A session**

Zoom Instructions

- Download Zoom
  - https://zoom.us/download
- If you cannot download Zoom, you can view the slides using an internet browser
  - Create a free Zoom account (https://zoom.us/signup)
  - Use a compatible browser (Firefox, IE or Edge)
  - View the webinar at https://success.zoom.us/wc/405388708/join
- If the material is not showing on your screen or if screen freezes
  - Key in Ctrl + F5 to do a hard refresh of your browser

Zoom Instructions (Cont'd)

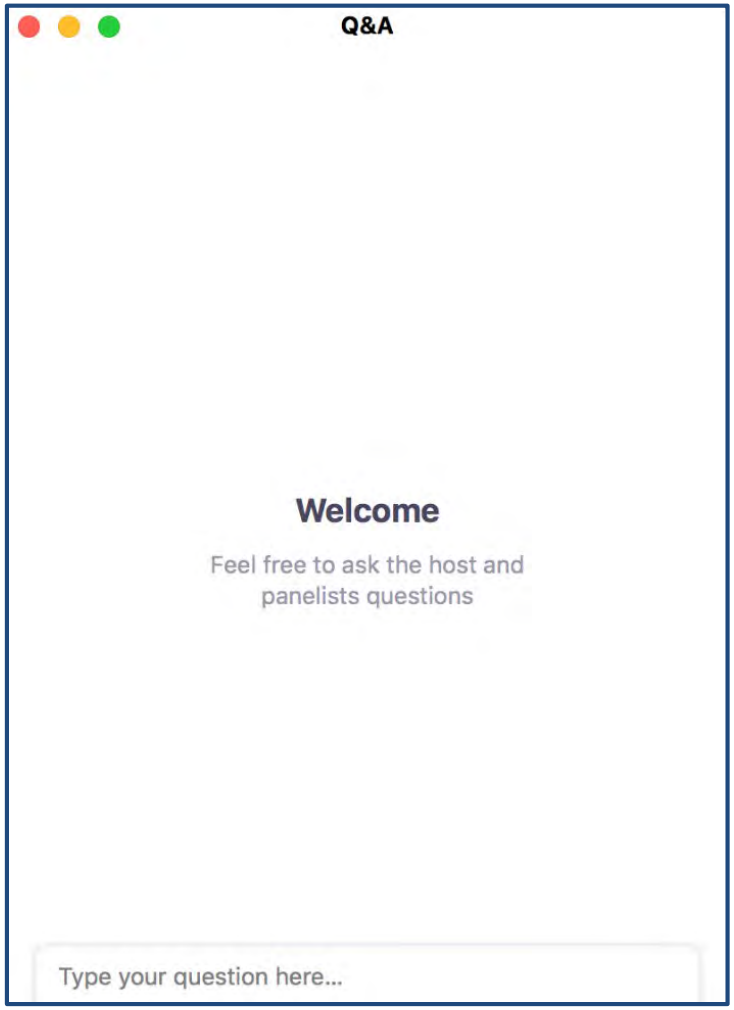
- If you are connecting to computer audio
  - Click the arrow next to the "Join Audio" button
  - Select test "Speaker and Microphone"
  - Follow prompts
- If you experience difficulties with the audio, call into the conference line
  - (669) 900-6833 or (929) 205-6099
  - Required webinar ID: 405-388-708

In Case of Continued Technical Difficulties

- Download a PDF of the slides at https://serdp-estcp.org/Tools-and-Training/Webinar-Series/06-04-2020 and call into the conference line
  - (669) 900-6833 or (929) 205-6099
  - Required webinar ID: 405-388-708
- We will also be live streaming the webinar on the SERDP and ESTCP YouTube channel
  - https://www.youtube.com/user/SERDPESTCP

How to Ask Questions

- Find the Q&A button on your control bar and type in your question(s)
- Make sure to add your organization name at the end of your question so that we can identify you during the Q&A sessions



SERDP and ESTCP Overview

Robin Nissan, Ph.D.
SERDP and ESTCP

SERDP

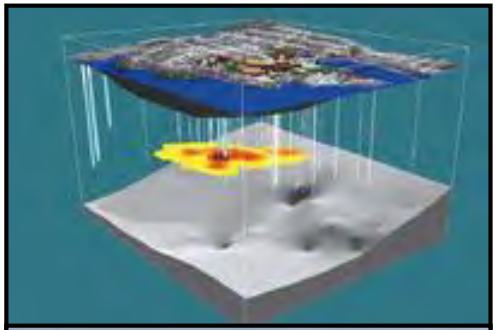
- Strategic Environmental Research and Development Program
- Established by Congress in FY 1991
  - DoD, DOE and EPA partnership
- SERDP is a requirements driven program which identifies high-priority environmental science and technology investment opportunities that address DoD requirements
  - Advanced technology development to address near term needs
  - Fundamental research to impact real world environmental management

ESTCP

- Environmental Security Technology Certification Program
- Demonstrate innovative cost-effective environmental and energy technologies
  - Capitalize on past investments
  - Transition technology out of the lab
- Promote implementation
  - Facilitate regulatory acceptance

Program Areas

- Environmental Restoration
- Installation Energy and Water
- Munitions Response
- Resource Conservation and Resiliency
- Weapons Systems and Platforms



Weapons Systems and Platforms

- Major focus areas
  - Surface engineering and structural materials
  - Energetic materials and munitions
  - Noise and emissions
  - Waste reduction and treatment in DoD operations
  - Lead free electronics

SERDP and ESTCP Webinar Series

Date	Topic
June 18, 2020	Advances in the Treatment of 1,4-Dioxane in Mixed Contaminant Plumes
July 9, 2020	Securing DoD Control Systems and Infrastructure from Cyber Threats
July 23, 2020	Predicting PFAS Fate and Transport in Subsurface Environments, and Treatment
August 20, 2020	Addressing Threatened and Endangered Species on DoD Lands
September 10, 2020	Approaches for Managing Contaminated Sediments
September 24, 2020	Munitions Response

For upcoming webinars, please visit

http://serdp-estcp.org/Tools-and-Training/Webinar-Series

SERDP DOD • EPA • DOE | ESTCP

Save the Date!

SERDP • ESTCP
SYMPOSIUM

A three-day symposium showcasing the latest technologies that enhance DoD's mission through improved environmental and energy performance

December 1-3, 2020
Washington, DC

Poster abstracts due July 15

Characterizing Shipboard Bilgewater Emulsions Using Macro- and Micro-Scale Flows

Cari Dutcher, Ph.D.
University of Minnesota, Twin Cities

SERDP DOD • EPA • DOE | ESTCP

Agenda

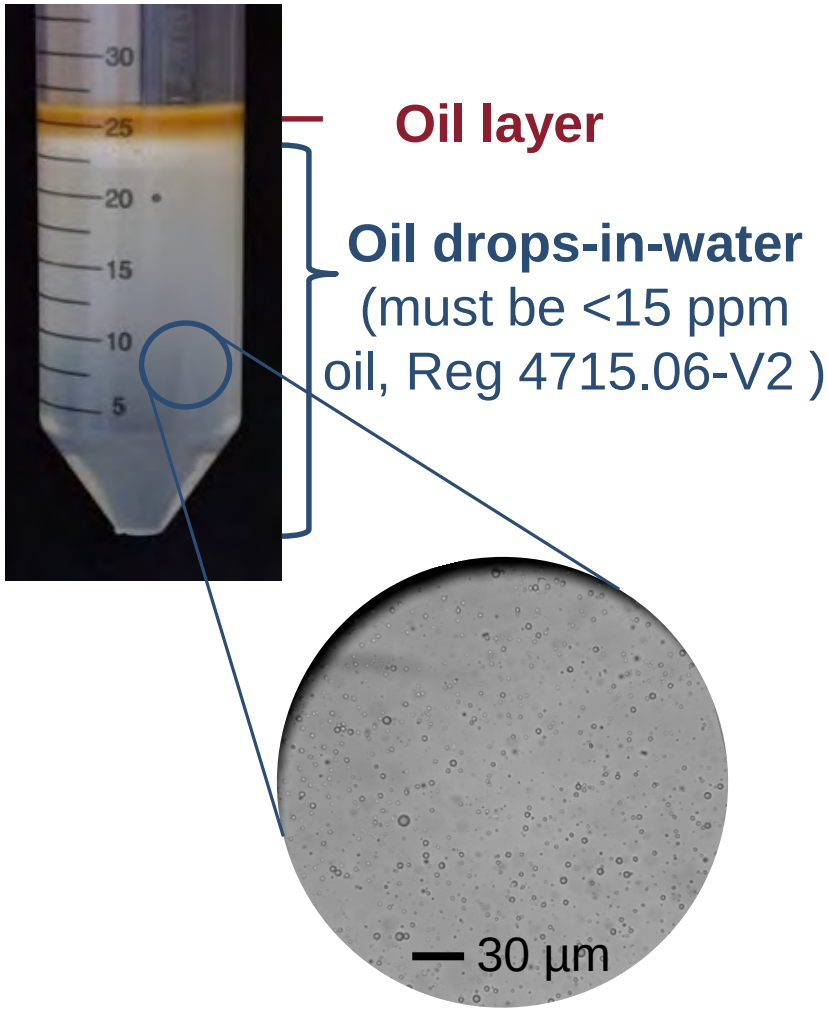
- Statement of need
- Background and key challenges
- Approaches
- Results
- Conclusions
- Benefits to DoD

Statement of Need

- Shipboard bilgewater emulsions (oily wastewater)
  - Engine oil, diesel fuels, other contaminants
  - >15 ppm oil cannot be discharged
  - Must be stored or treated shipboard
- Need improved mitigation strategies
  - To increase the volume of water discharged
  - Improved strategies enabled by improved fundamental understanding

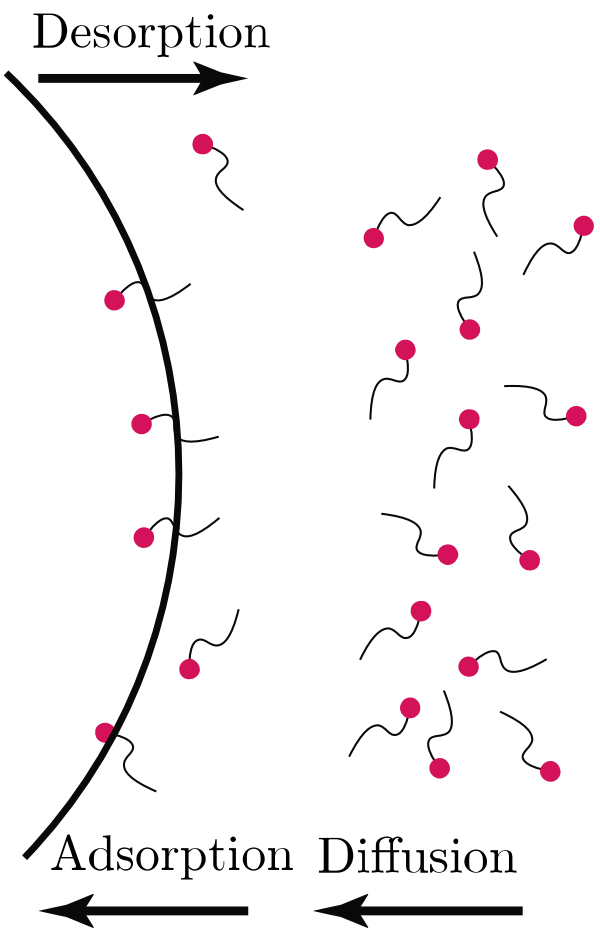
Technical Background

- Primary treatment for large drops (> 30 µm)
  - Drops relatively easy to separate
  - Big enough to readily settle or wet surfaces
- Secondary treatment for small drops (< 30 µm)
  - Much more difficult to separate
  - Drops too small to settle without aid



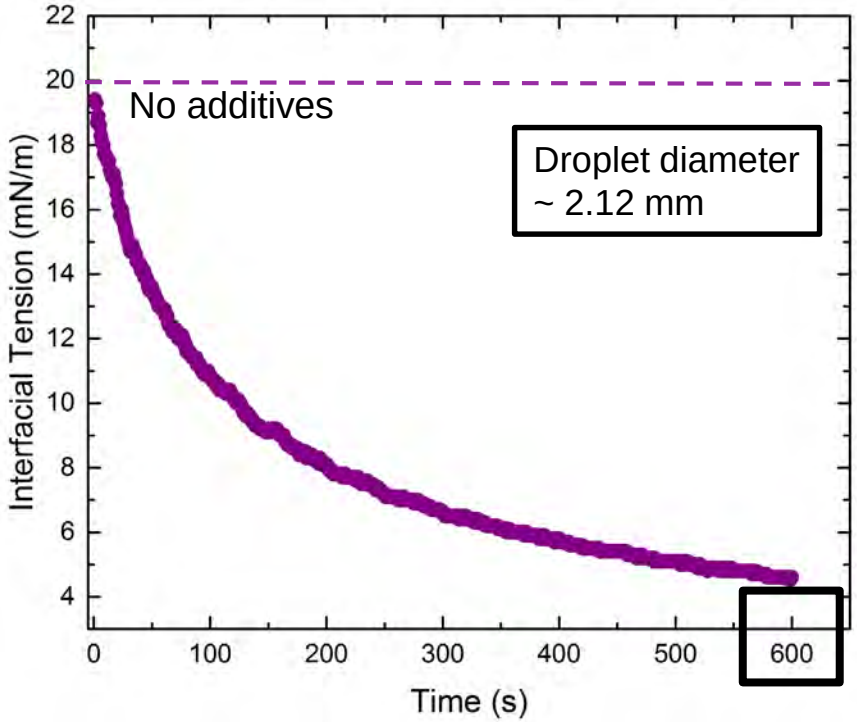
Challenge 1: Chemical Stabilization

- Surfactants from cleaning agents stabilize emulsions
- Detergent molecules move to interfaces
  - Lower interfacial tension ("IFT")
  - Lower surface energy
  - More difficult to phase separate

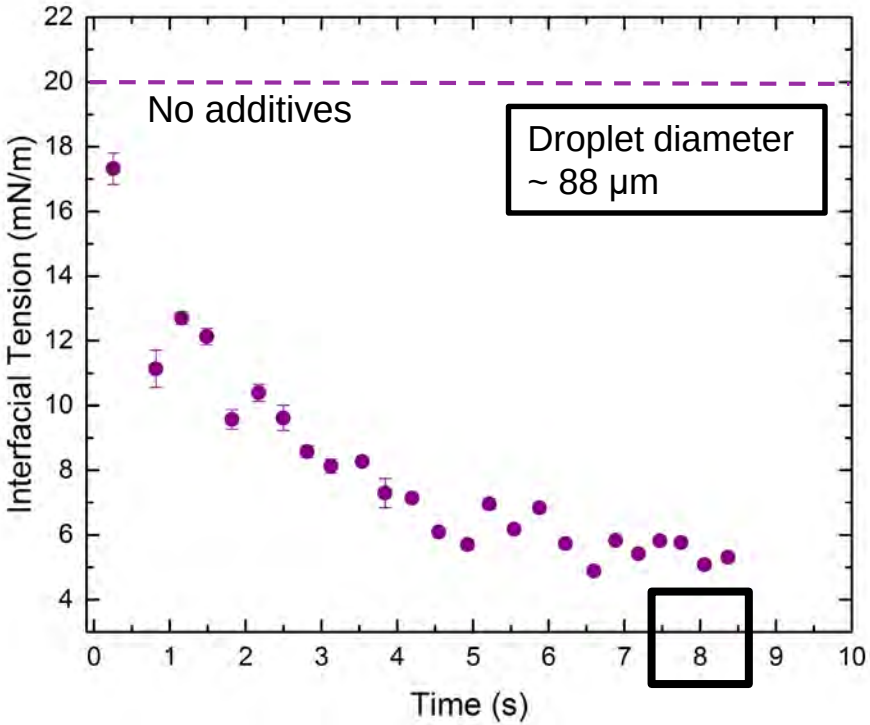


Challenge 2: Size Dependence

Bulk Pendant Drop Data



Microfluidic Data



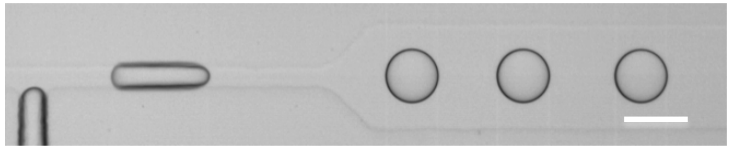
Surfactant stabilization time depends on droplet size
Transition from diffusion- to kinetic- driven process

***Source**: Narayan et al., Energy and Fuels (2018)*

Technical Approach

Microscale Flows

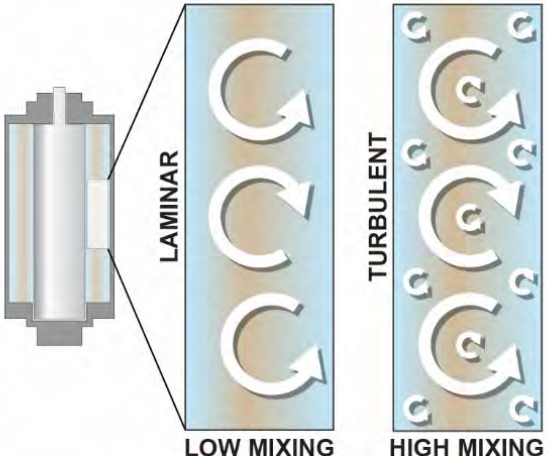
- Study individual droplets
- Droplet microfluidics
  - High-throughput
  - Monodispersed droplets
  - Relevant droplet sizes
  - Easy manipulation of drops



Microfluidic water droplet generation in oil
(Scale bar is 100 µm)

Macroscale Flows

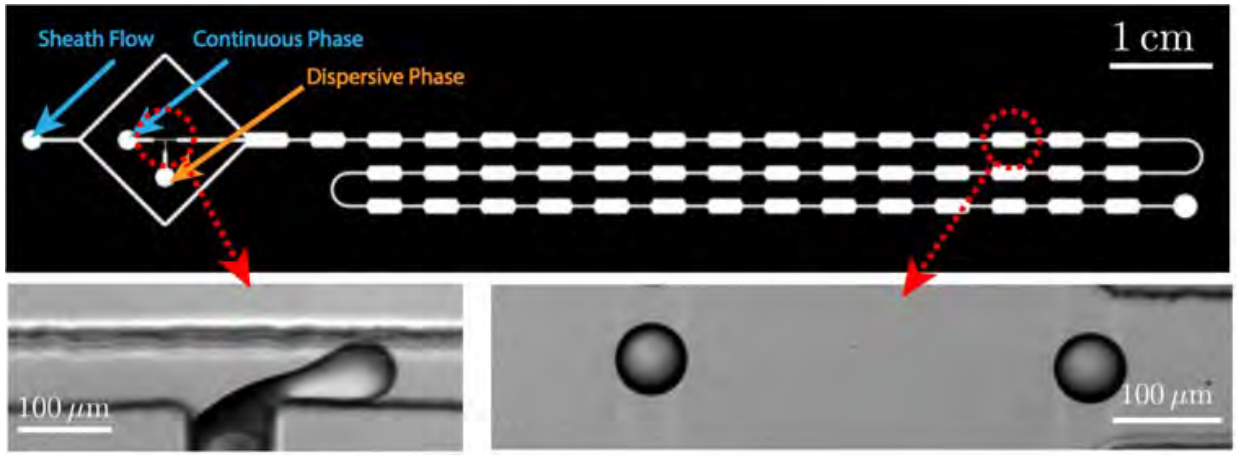
- Study bulk emulsions
- Taylor-Couette flows
  - Well-characterized
  - Many flow types
  - Easy flow visualization

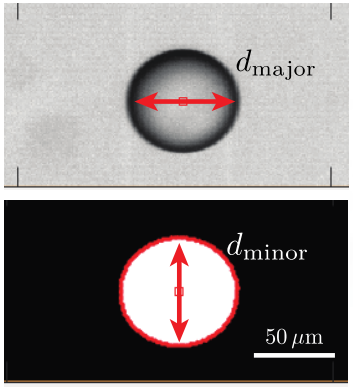


***Source**: Metaxas et al., Soft Matter (2018)*

Microscale Measurements

- Create droplets on a microfluidic chip
- Change the flow field around the drop
- Measure the droplet shape response





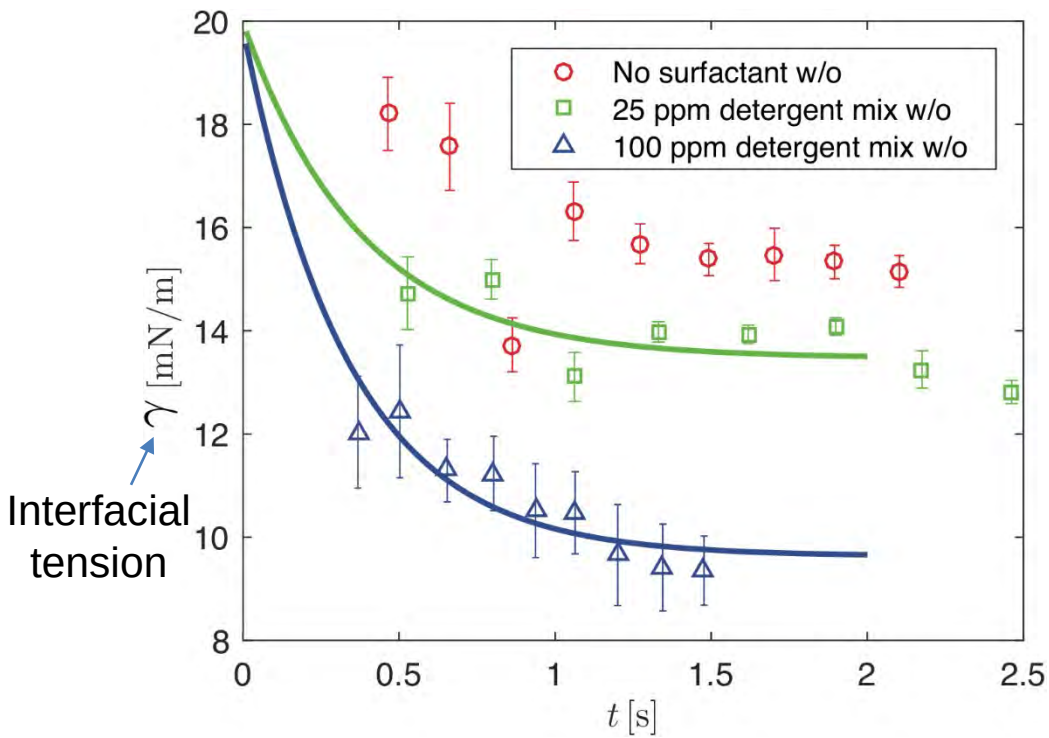
Source: *Chen and Dutcher, Soft Matter (2020)*

Simulated Oil-Water Systems

Simulated Bilge Oil Mix	Detergent Mix
50% - Diesel Fuel Marine (MIL-PRF-16884N)	50% - Type 1 General Purpose Detergent (MIL-D-16791G(1))
25% - 2190 TEP Steam Lube Oil (MIL-PRF-17331K)	25% - Commercial Detergent Tide Ultra (liquid)
25% - 9250 Diesel Lube Oil (MIL-PRF-9000L)	25% - Degreasing Solvent (MIL-PRF-680C, Type III)

Simulated Oil-Water Systems

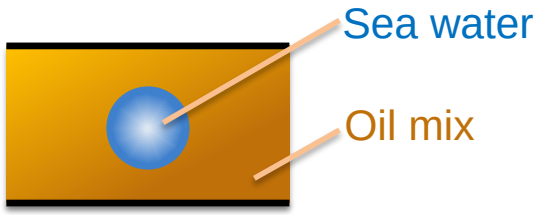
- Size dependence
  - Decrease in IFT ~10x faster for micrometer droplets
- "Simple" oil-water still complex
  - Even the diesel fuel and lubricating oils have surfactants



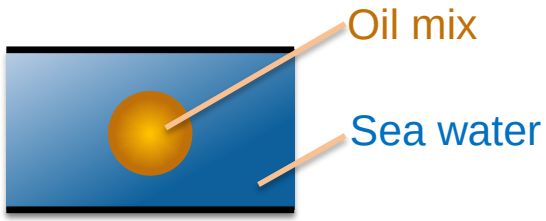
***Source**: Chen and Dutcher, Soft Matter (2020)*

Simulated Oil-Water Systems

- Phase matters
  - Dry vs. wet bilge

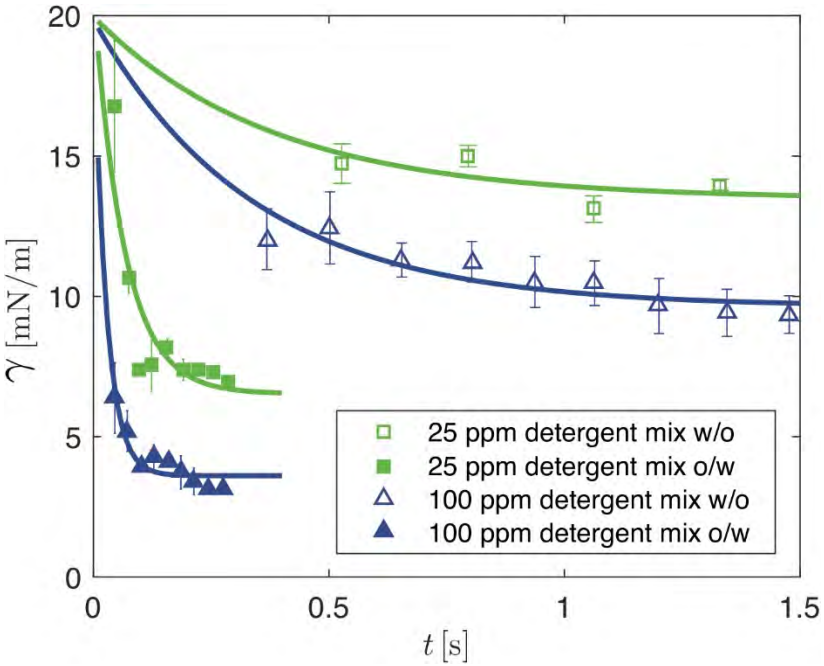


(w/o, open symbols)



(o/w, closed symbols)

- Phase dependence only seen with μm droplets

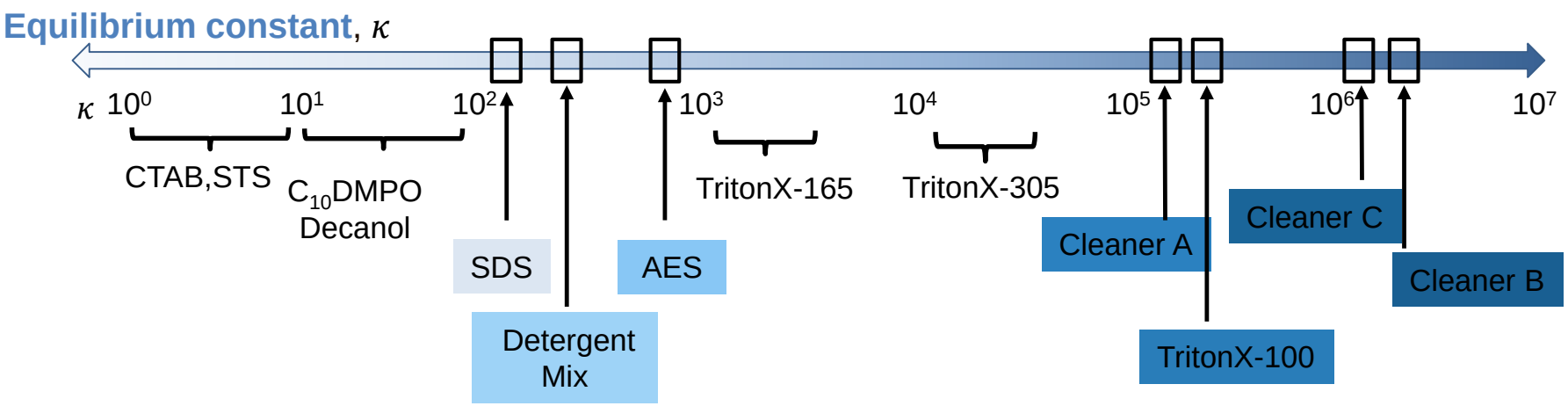


***Source**: Chen and Dutcher, Soft Matter (2020)*

Surface Affinity from Pendant Drop

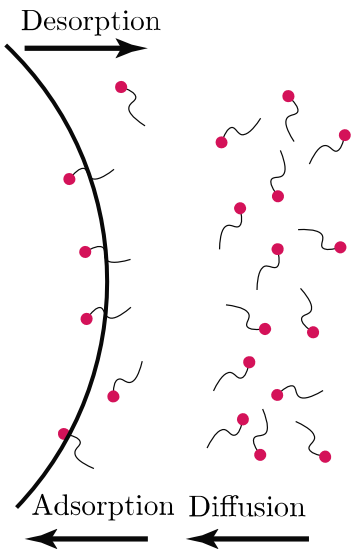
Surfactant	M_w (g/mol)	Type
Detergent Mix	300	Anionic
AES	420	Anionic
TritonX-100	625	Non-ionic
SDS	288	Anionic
Cleaner A	617	Non-ionic
Cleaner B	214	Non-ionic
Cleaner C	293	Non-ionic + Anionic

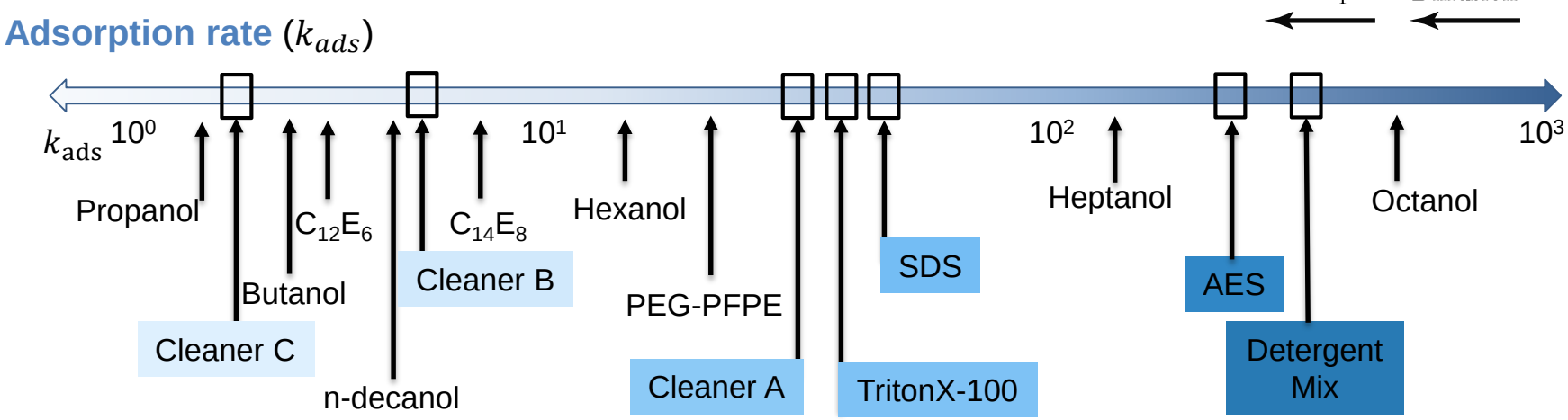
- Macroscale measurements
  - Critical micelle concentration (CMC)
  - Maximum surface coverage
  - Equilibrium constant
  - Diffusivity



Adsorption Rates from Microfluidics

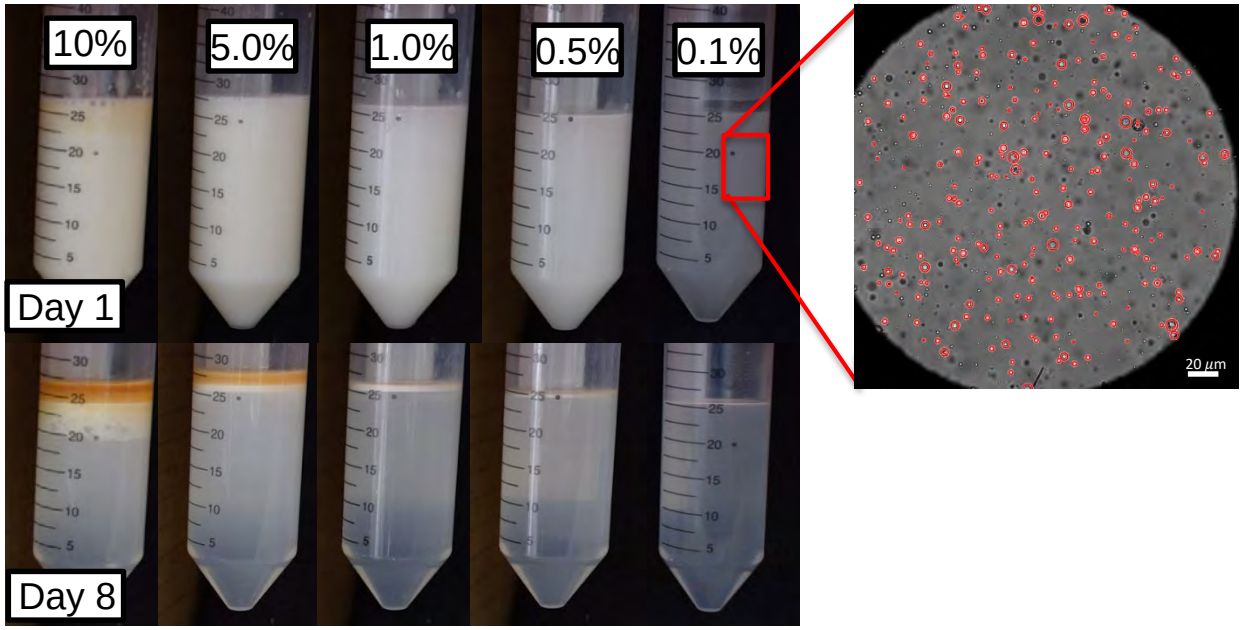
- Microscale measurements
  - Adsorption rates
  - Desorption rates





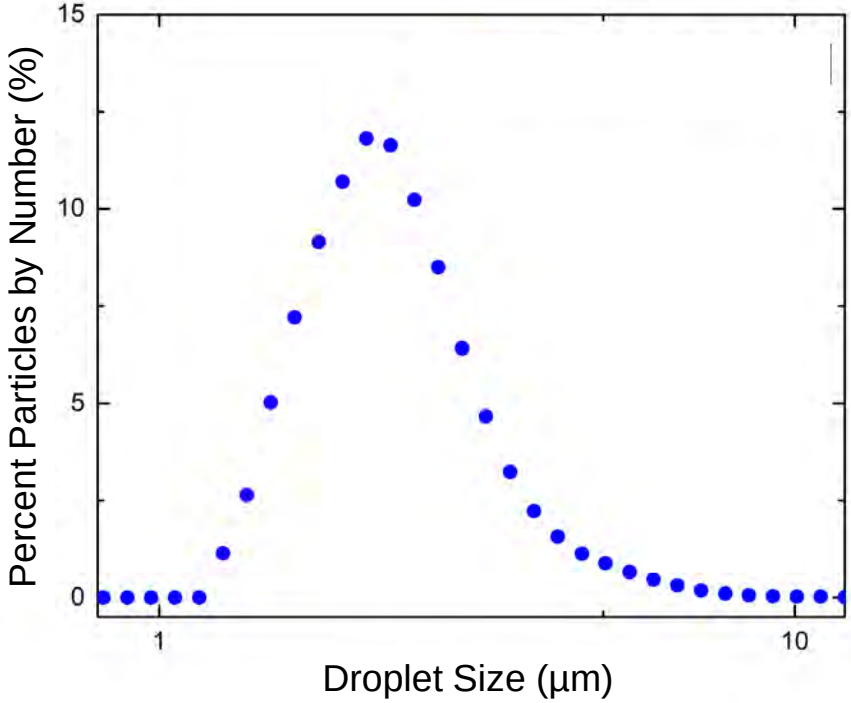
Macroscale Bulk Stability

- Observable oil separation and turbidity change
- Used to find destabilization timescales

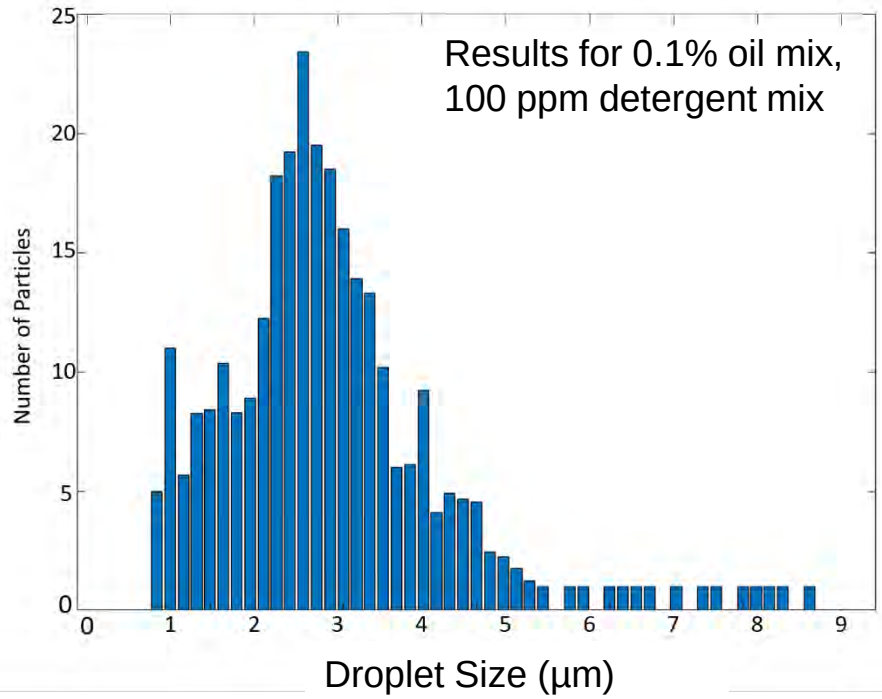


Changes in Size Distribution

Laser Diffraction



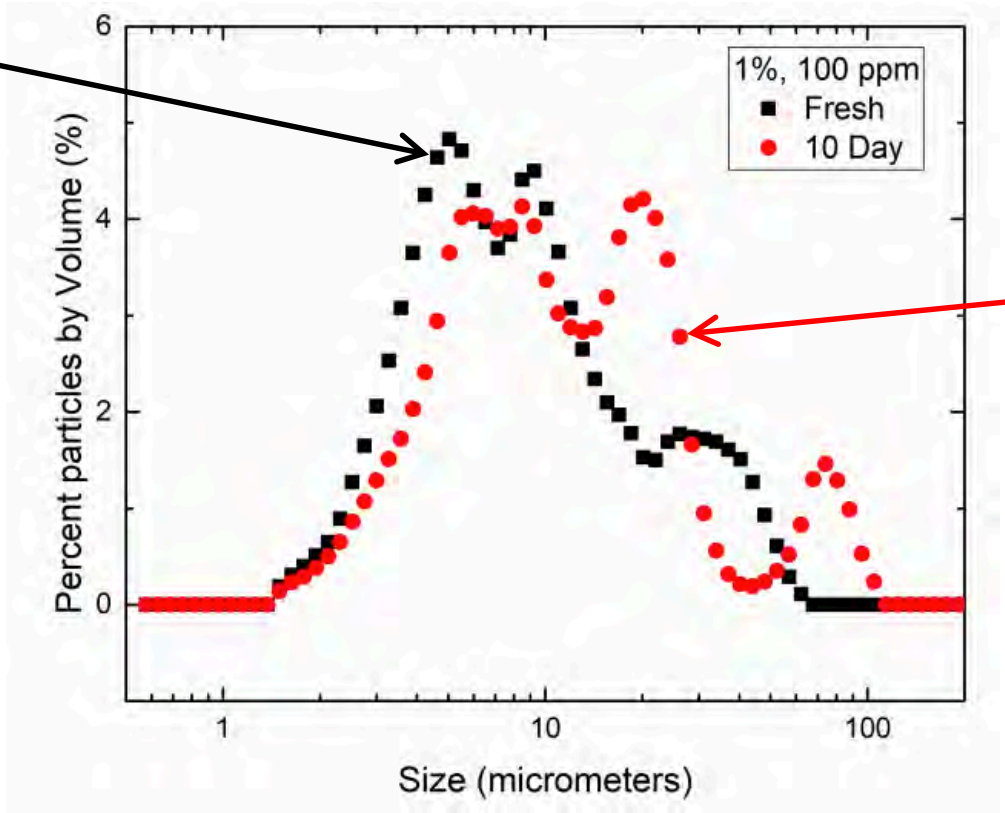
Optical Microscopy

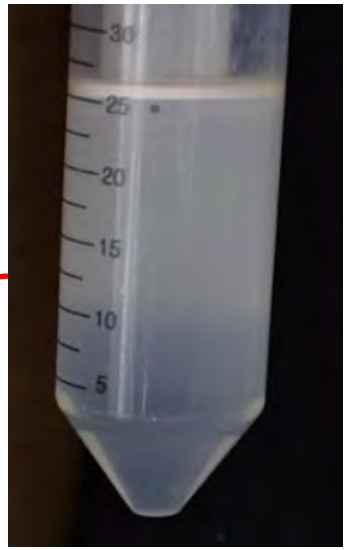


Similar results for both methods (1 - 10 micrometers)
Size will depend on preparation (e.g., homogenizer)

Changes in Size Distribution with Age

Fresh: More droplets, more scattered light



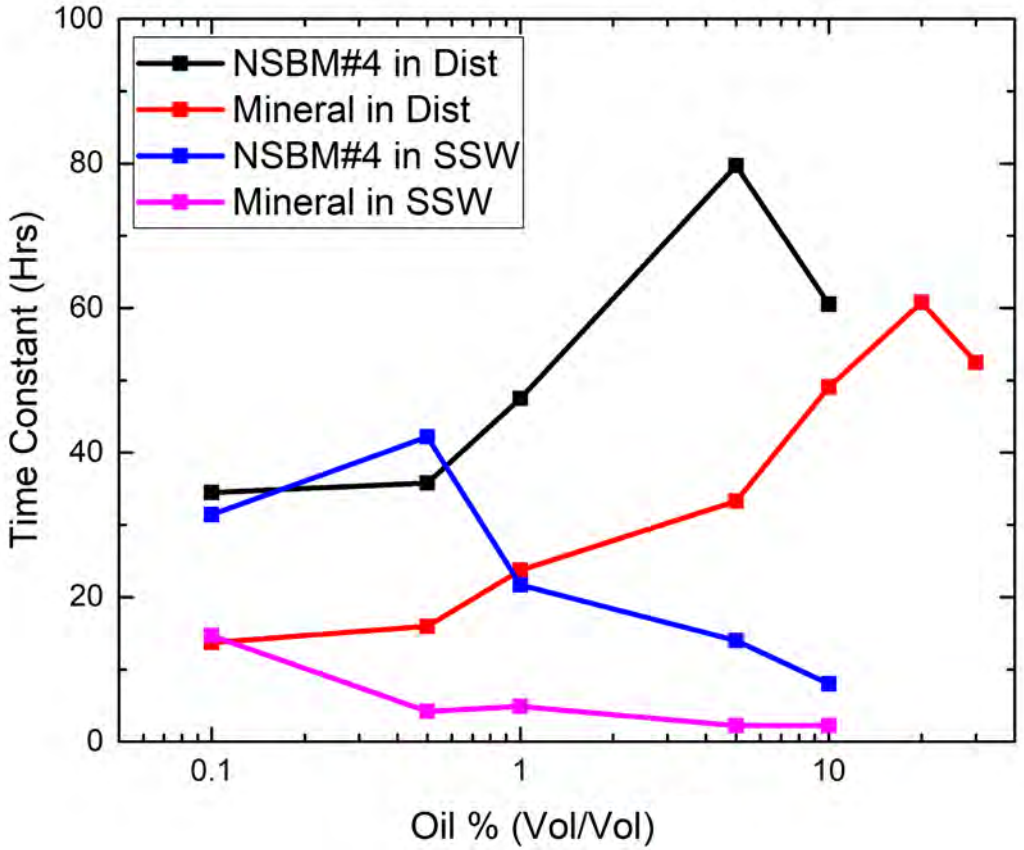


10 Days: Fewer droplets, less scattered light

Partial destabilization over long periods of time

Destabilization rates depend on composition

Changes Due to Oil and Salt



Mineral oil less stable than simulated bilgewater oil

Salt causes significant destabilization

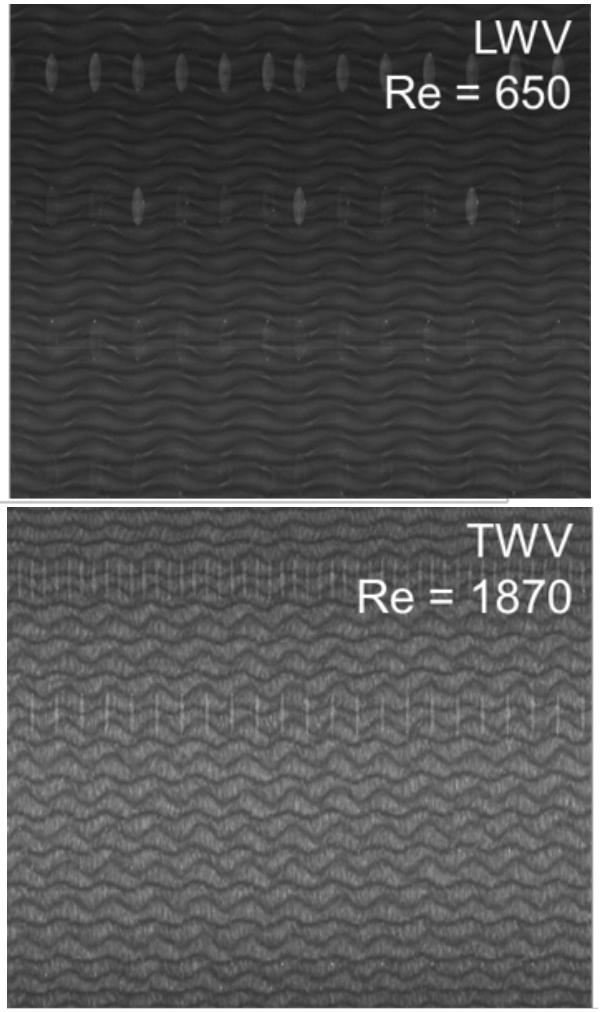
Changes Due to Simple Shear

- Shear can destabilize emulsions
- Viscosity, turbidity, size distribution
- Most pronounced at >10 wt% oil
- Not observable at <1 wt% oil
  - Up to 2000 1/s
  - Simulated bilgewater oil/detergent mixes
  - With and without sea salts

AR-G2 TA Instrument

Changes Due to Complex Flows

- Taylor-Couette flows
  - Laminar flow states (LWV)
  - Turbulent flow states (TWV)
- Destabilization occurred for <1 wt% oil systems
  - Minimal destabilization for LWV flows
  - Pronounced destabilization for TWV flows



***Source**: Metaxas et al., Soft Matter (2018)*

Conclusions

- Measurements at correct length scales
  - Surfactant transport depends on interfacial curvature
  - Emulsion stability depends on droplet size distributions
- Destabilization rates variable
  - Composition: Surfactant type, oil%, salt
  - Mixing: Flow type and turbulent intensity

Benefits to DoD

- Bilgewater mitigation needs
  - < 15 ppm oil
  - Enhanced separation of oil from water
- New measurement platforms
- Database of dynamic properties
  - Surfactant properties
  - Emulsion stability
- Inform operation and mitigation strategies

Acknowledgements

- Dr. Yun Chen
  - Postdoctoral scholar
  - Microfluidic measurements, isotherm analysis
- Mr. Thomas Neumiller
  - Mechanical engineering graduate student
  - Bulk stability analysis, Taylor-Couette flows

For additional information, please visit

www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Waste-Reduction-and-Treatment-in-DoD-Operations/WP18-1031

Speaker Contact Information

cdutcher@umn.edu; 612-624-0428

SERDP DOD • EPA • DOE | ESTCP

Q&A Session 1

SERDP DOD • EPA • DOE | ESTCP

Emulsion Characterization Study For Improved Bilgewater Treatment and Management

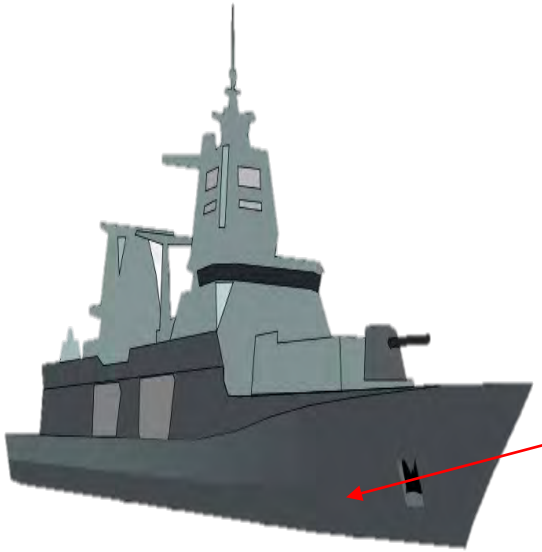
Danielle M. Paynter
Naval Surface Warfare Center
Carderock Division

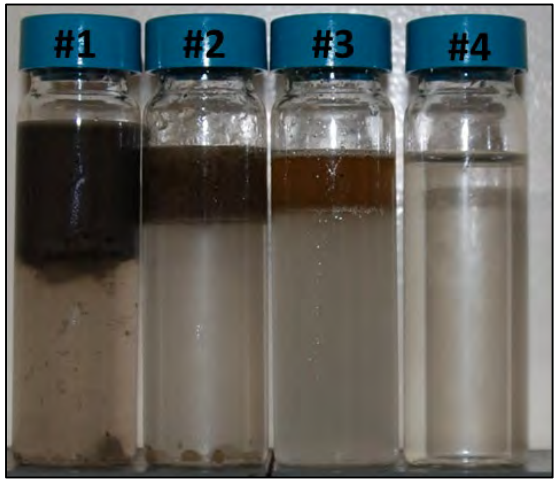
Agenda

- Introduction to bilgewater
- The problem with bilgewater emulsions
- Goals and objectives
- Characterizing shipboard cleaners
- Emulsion stability
  - Cleaner properties
  - Environmental impacts
  - Fuel additives
- Conclusions and next steps

Introduction to Bilgewater

- Bilge – Lowest part of hull where liquid drains from the interior spaces and upper decks of the vessel
- Bilgewater composition
  - Highly variable
  - Dependent upon shipboard tasks
  - Can lead to the creation of oil-in-water emulsions





Bilgewater samples from four Navy ships

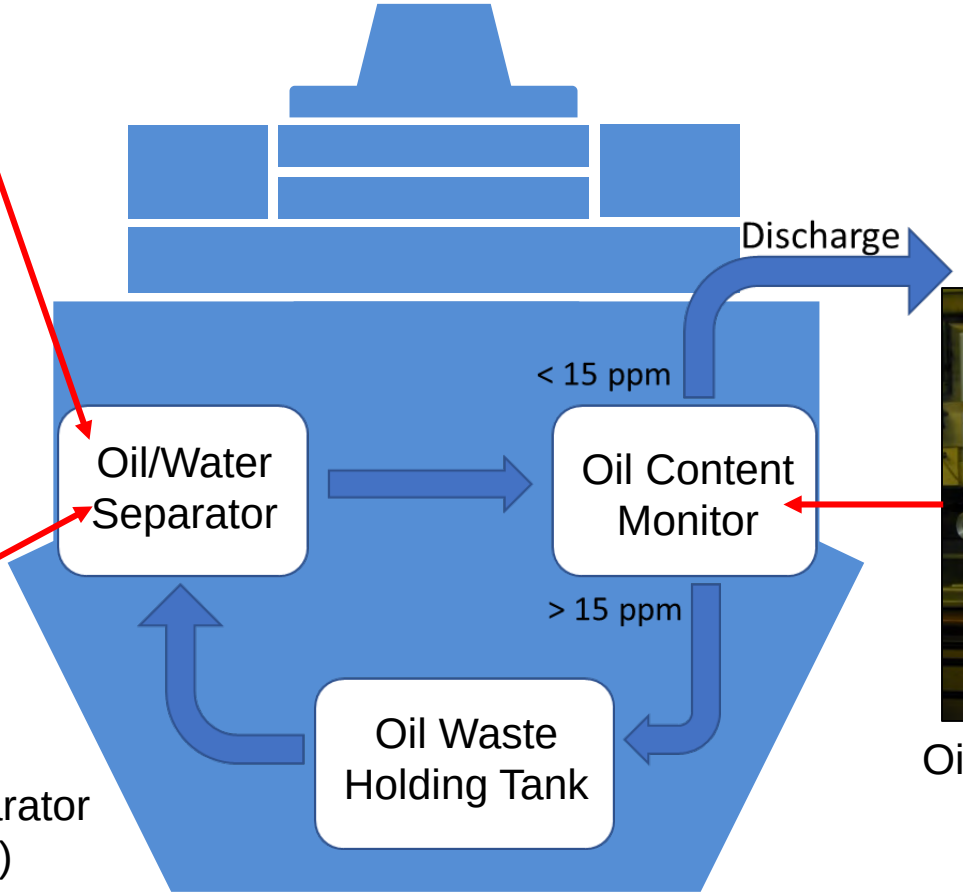
Bilgewater Discharge Regulations

- Oil discharge limited to 15 parts per million (ppm)
  - Environmental Protection Agency (EPA) Clean Water Act (U.S. Code Title 33 Chapter 40)
  - Department of Defense Regulation (DoD 4715.06 Volumes 2 and 4)
  - Chief of Naval Operations Instruction (OPNAVINST M-5090.1)

Oil Pollution Abatement (OPA) System

Gravity-Coalescence Oil/Water Separator

Membrane Oil/Water Separator (Secondary Treatment)



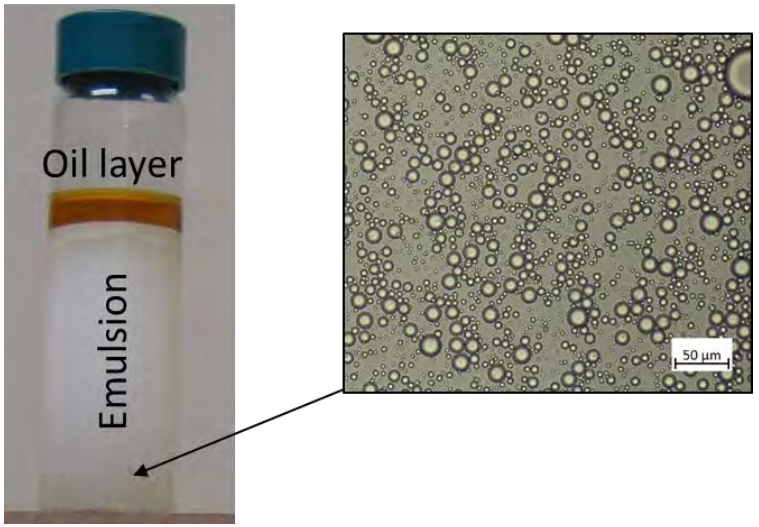
Oil Content Monitor

Collect, hold, treat, and analyze oily waste on board ships

The Problem With Bilgewater Emulsions

- Surfactants or cleaners used in daily shipboard activities
  - Engine, deck, surface cleanings
- Washed surfaces create a wastestream
  - Drains to bilge
- Surfactants/solids → emulsion formation
- Droplets <10 µm are suspended for extended weeks to years
- Small droplets in emulsions challenge traditional treatment systems

Anatomy of an Emulsion



Improved understanding of bilgewater emulsions will inform treatment system selection, operation profiles, and problematic cleaners

Goals and Objectives

Advance the current understanding of chemically stable emulsions formed in Armed Forces vessels through emulsion characterization and modeling analysis

Task 1
Scoping Study for Review of Armed Forces Vessels Oil-in-Water Emulsions

- Literature, technical, and regulation review
- Shipboard personnel interviews
- Shipboard cleaner procurement query and characterization

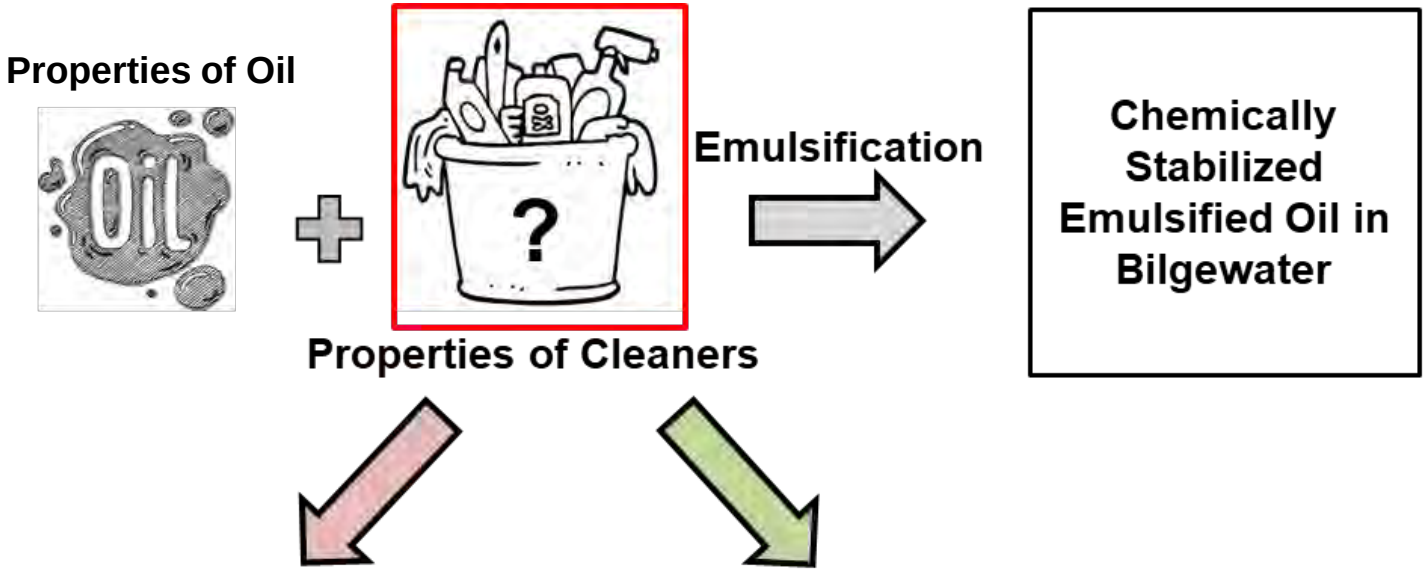
Task 2
Characterization of Prepared and Extracted Bilgewater Emulsions

- Impact of cleaner properties on emulsion stability
- Environmental impacts on emulsion stability
- Impact fuel additives on emulsion stability

Task 3
Data Analysis and Interpretation

- Model development for predicting emulsion stability

Preventing Bilgewater Emulsions



Structural Properties

- Hydrophilic/Lipophilic Balance (HLB)
- Surfactant interactions
- Surfactant lifetime
- Chemical composition

Physical Properties

- Critical Micelle Concentration (CMC)
- Interfacial Tension
- Hydrophilic/Lipophilic Deviation (HLD)
- Zeta Potential

How to identify properties of cleaners that would reduce emulsion stability?

Shipboard Cleaners

- Identified and characterized most common Navy ship cleaning/surfactant based products
- Properties vary widely including:
  - CMC
  - Surface tension (ST)
  - Interfacial tension (IFT) with Navy Standard Bilge Mix (NSBM) #4
  - Micelle size
  - Zeta potential

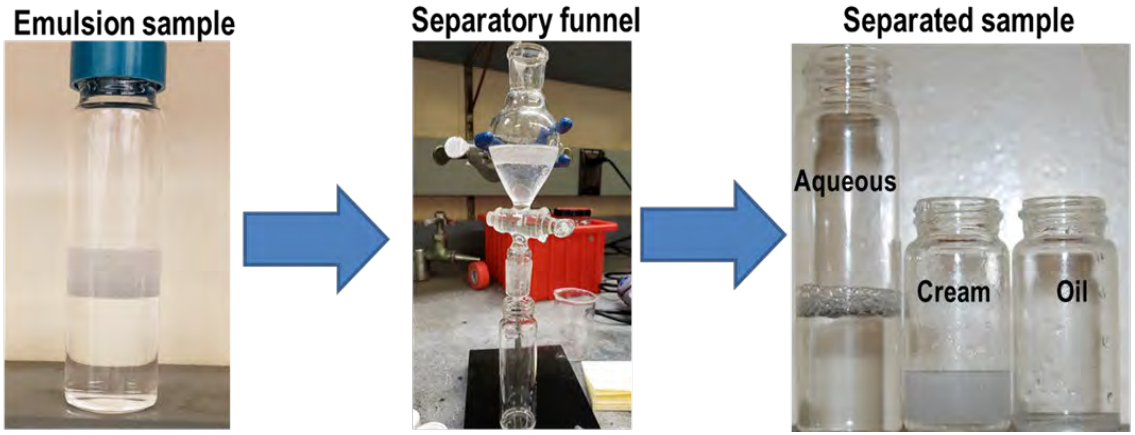
Cleaner	Primary surfactants
AFFF 6% (Chem Guard)	• Flourosurfactant (e.g. Capstone 1157)
B&B™ 3100 (Vantage)	• Cocamide diethanolamine • 1-buoxyethanol (alcohol ethoxylate)
Super Blast Off (Elsco Inter. Inc.)	• Cocamide diethanolamine
Calla 855 (Zip-Chem Products)	• Alcohol ethoxylate (c10-c14) • Cocamide diethanolamine • Capriloamphorionate
Power Green (LHB Industries)	• Surfactant blend
PRC Deck Cleaner (Werth Sanitary Supply Co. Inc.)	• Alcohol ethoxylate
Ecolab Solid Surge Plus NP (Ecolab # 6117905)	• Alcohol ethoxylate (c12-16)
Type 1 Detergent (MILSPEC: MIL-D-16791)	• Alkyl aryl polyether alcohol

Typical Shipboard Cleaner Composition

- Builders (50%)
  - Alter water chemistry
  - Improve surfactant efficiency (buffers and softeners)
- Surfactants (15%)
  - Emulsification of soil/oils into water
  - Improving wetting
- Bleach (10%)
  - Oxidize organic stains
- Other components (< 2%)
  - Enzymes
  - Foam regulators
  - Corrosion inhibitors
  - Optical brighteners
  - Fragrances

Cleaner Properties and Emulsion Stability

- Motivation
  - Understand the effect of cleaner properties on stability and formation of macroemulsion
- Approach
  - Study prepared emulsion systems of varying properties for both the reference surfactants and shipboard cleaners
- Analysis
  - Bulk emulsion stability
  - Droplet size analysis

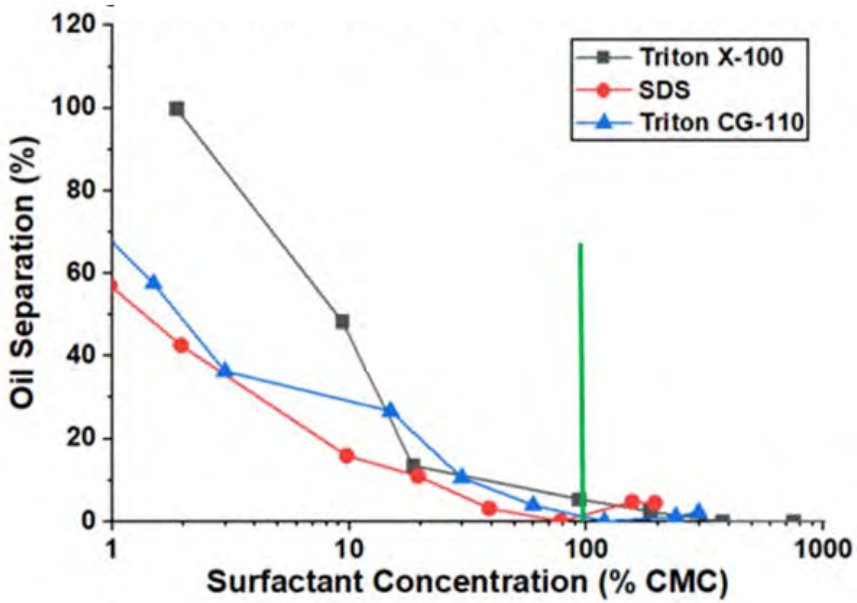


Role of CMC on Emulsion Stability

CMC Based on ST for Reference Surfactants

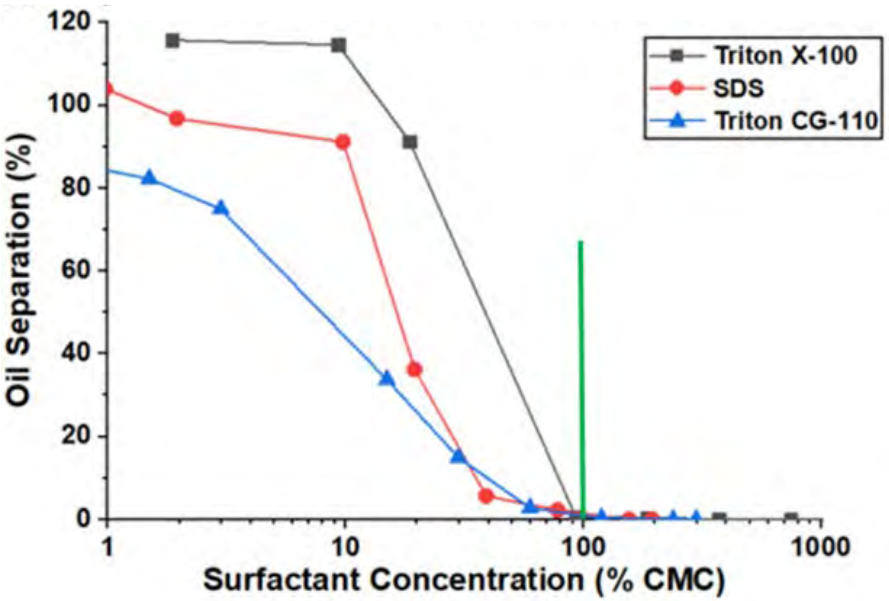
High Intensity Homogenization

20% Mineral Oil



Low Intensity Homogenization

20% Mineral Oil

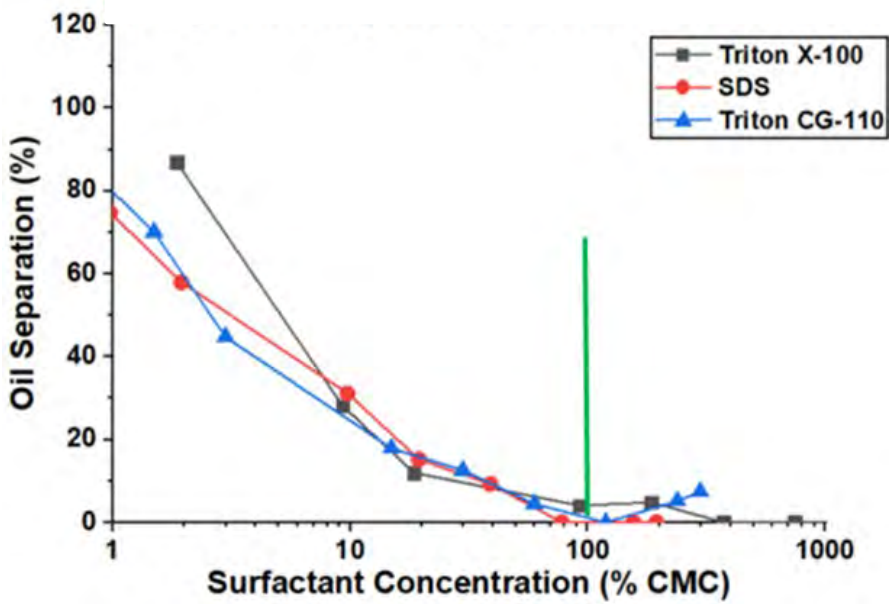


Role of CMC on Emulsion Stability

CMC Based on ST for Reference Surfactants

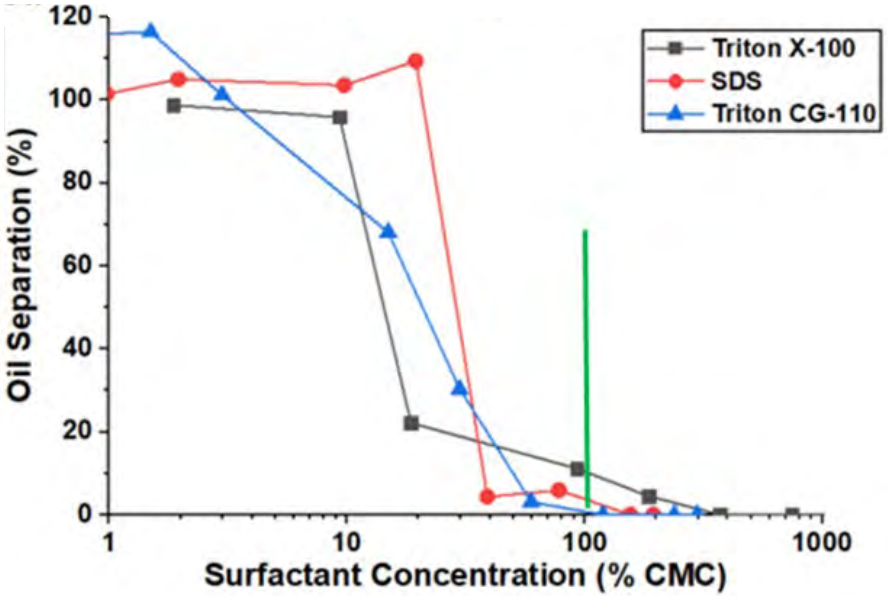
High Intensity Homogenization

10% Mineral Oil



Low Intensity Homogenization

10% Mineral Oil



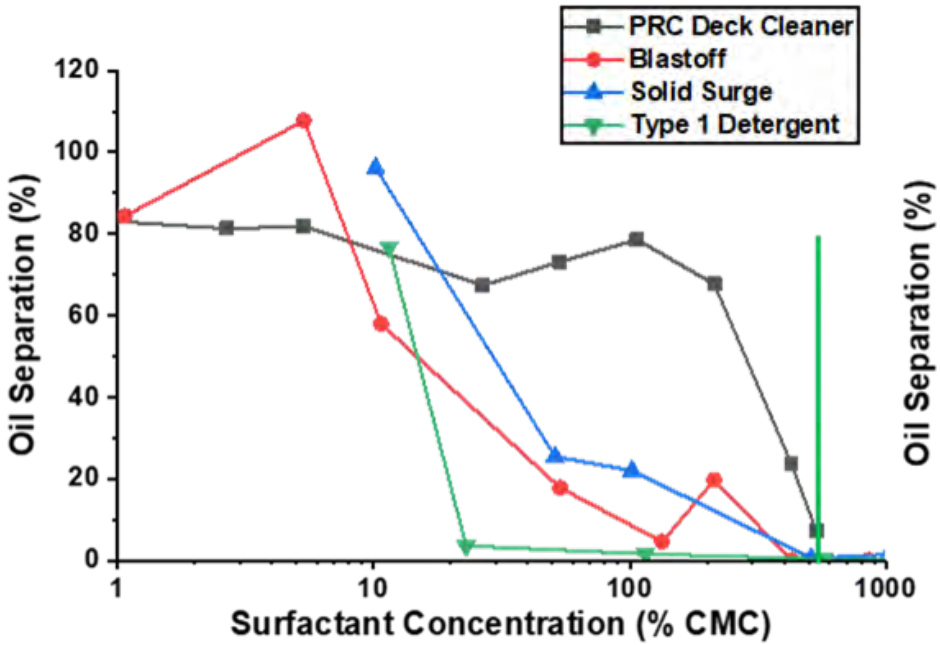
CMC inflection point between partially coalesced and fully emulsified systems observed in reference surfactants for all tested conditions

Role of CMC on Emulsion Stability

CMC Based on ST for Shipboard Cleaners

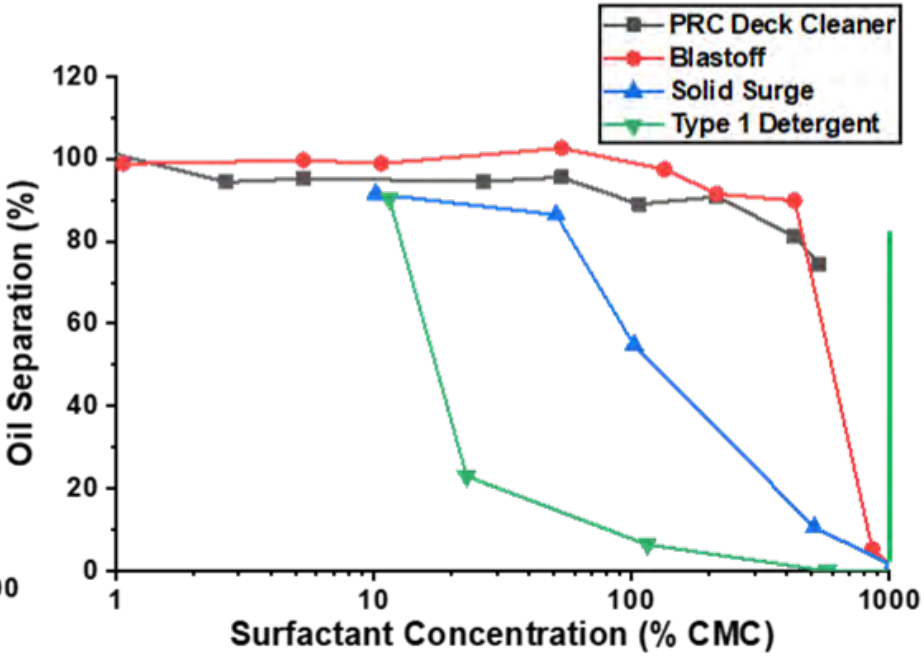
High Intensity Homogenization

20% Mineral Oil



Low Intensity Homogenization

20% Mineral Oil

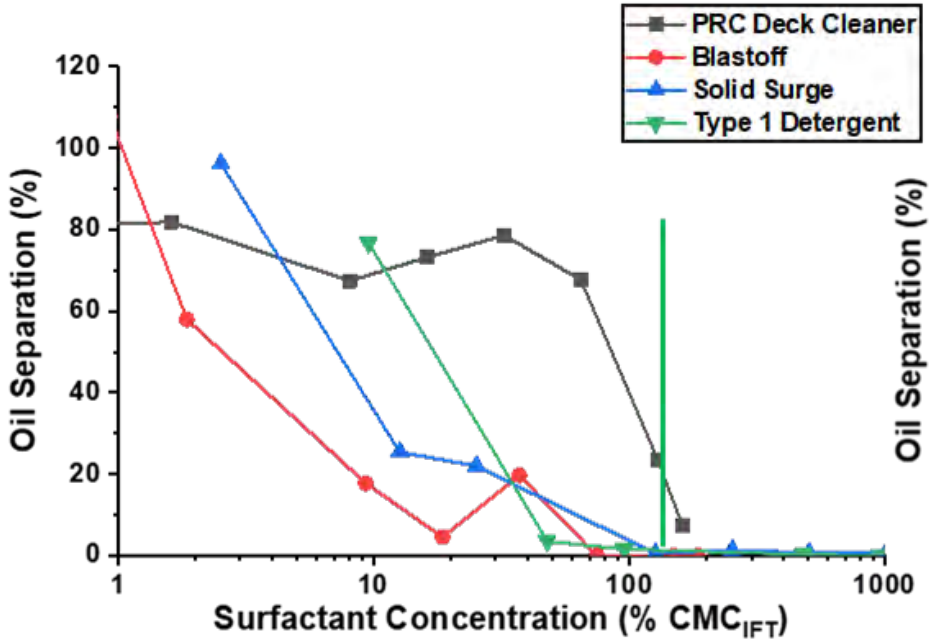


Role of CMC on Emulsion Stability

CMC Based on IFT for Shipboard Cleaners

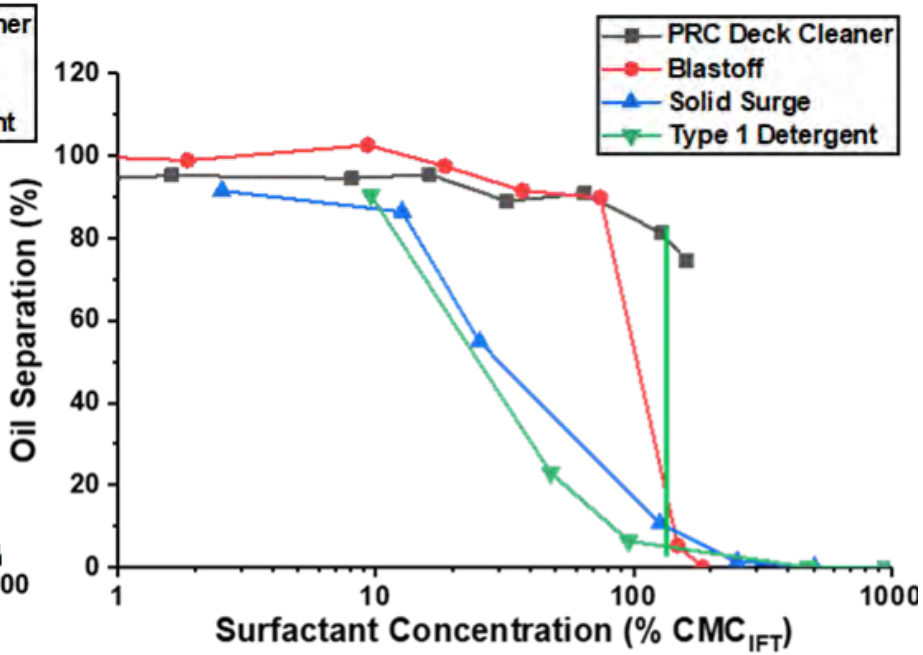
High Intensity Homogenization

20% Mineral Oil



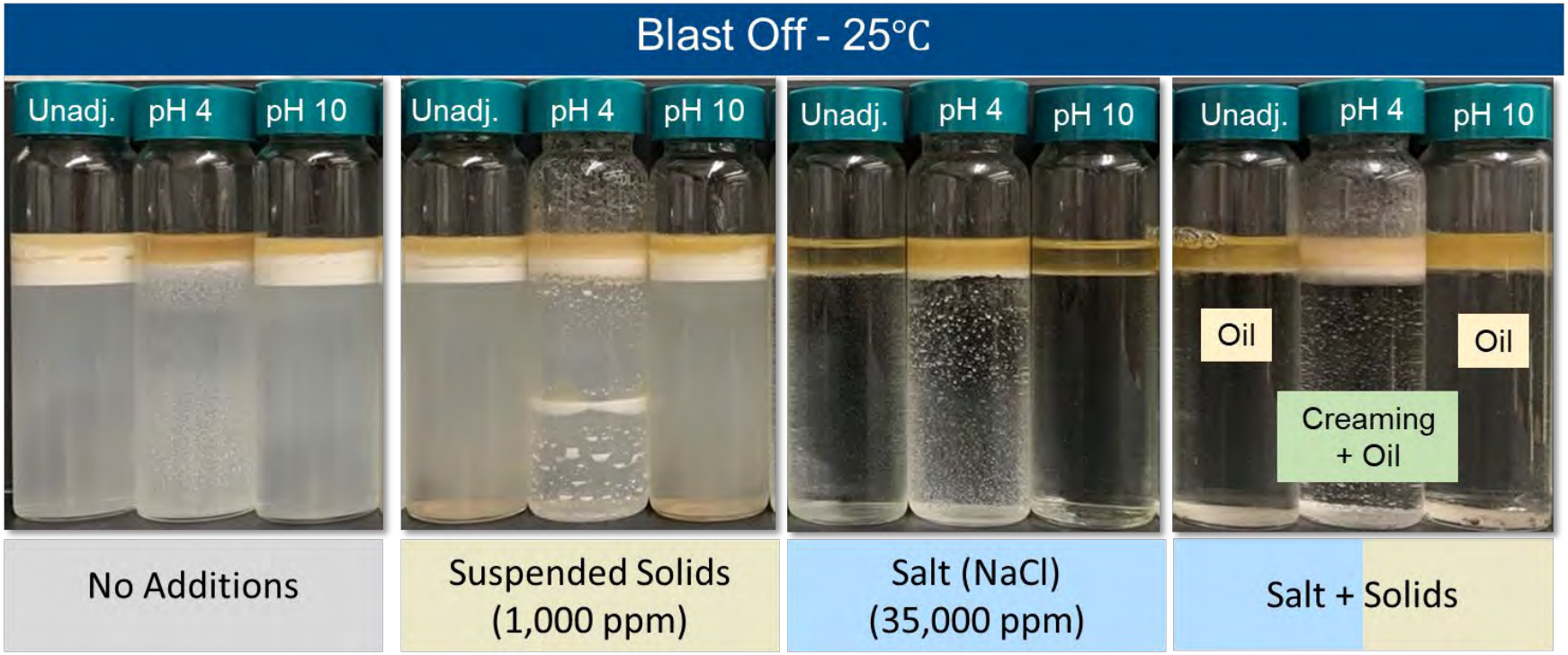
Low Intensity Homogenization

20% Mineral Oil

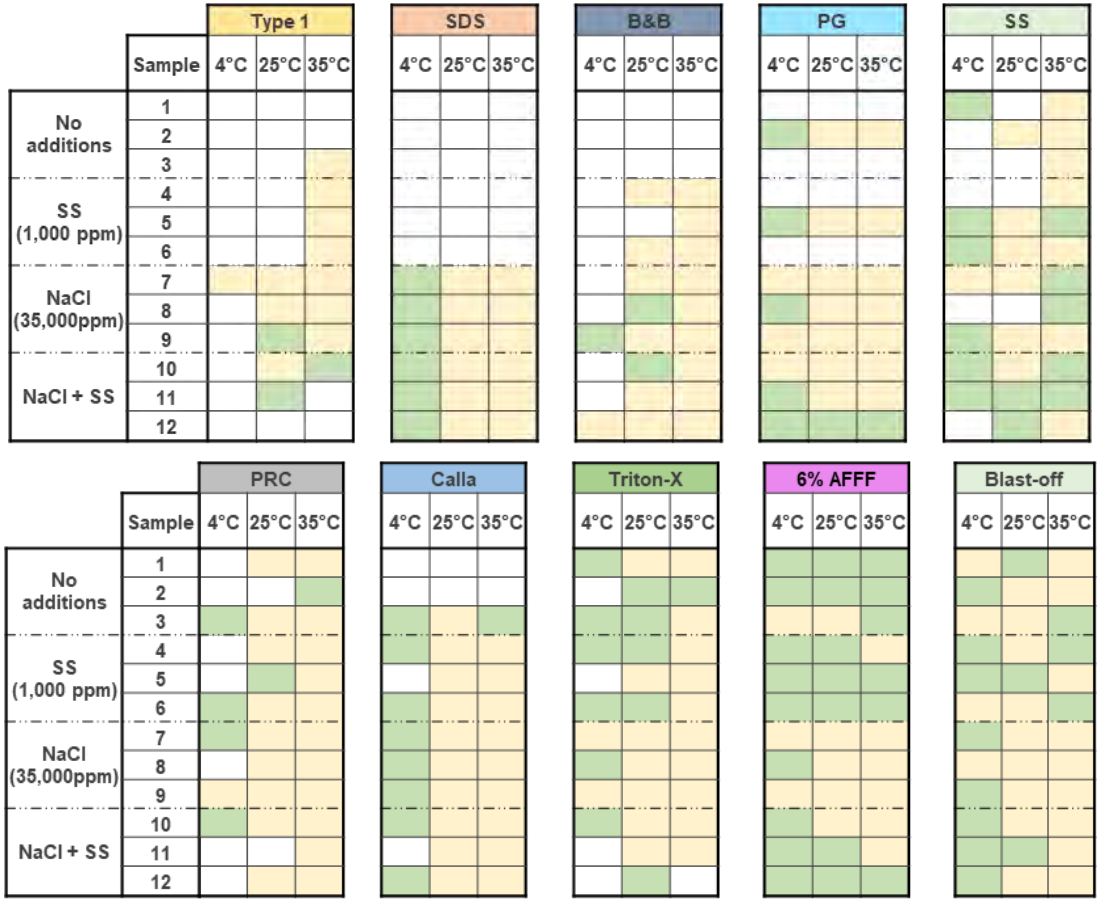


Surfactants and builders behave differently at oil-water (IFT) vs. air-water (ST) interfaces, but CMC based on IFT measurements shifted the inflection point back to 100% CMC

Environmental Impacts on Emulsion Stability



Environmental Impacts on Emulsion Stability

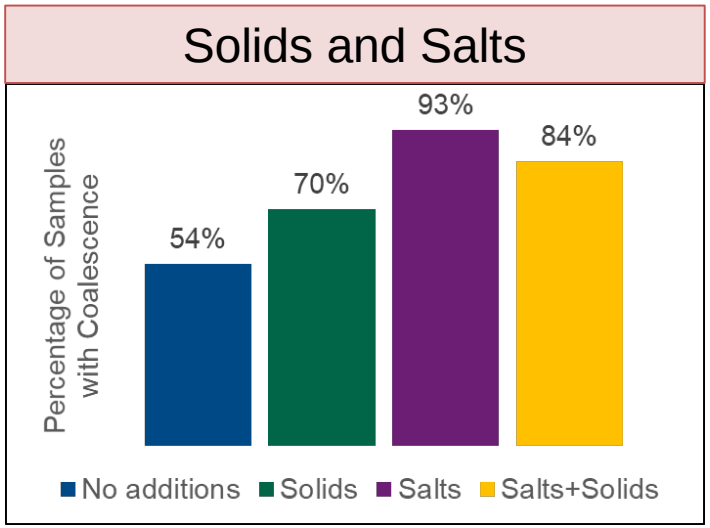


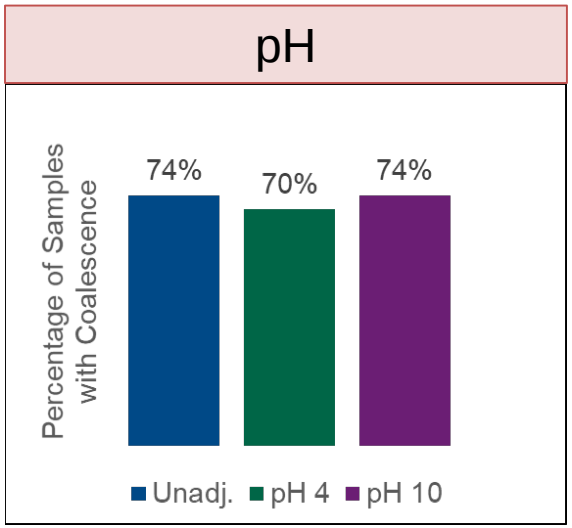
Legend

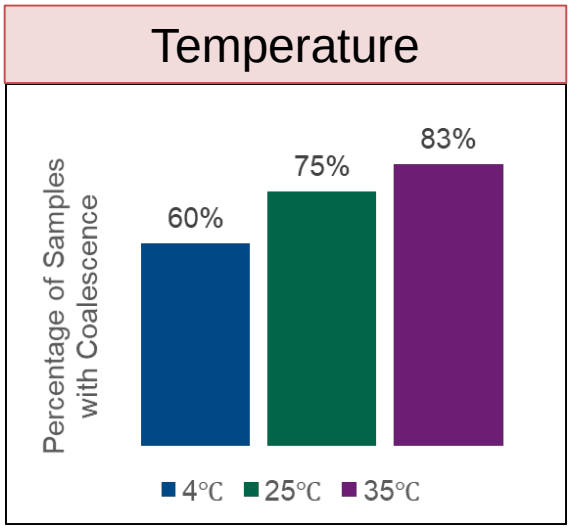
- Oil
- Creaming + Oil

Builders and other components in commercial cleaners have a significant impact on emulsion stability

Environmental Impacts on Emulsion Stability







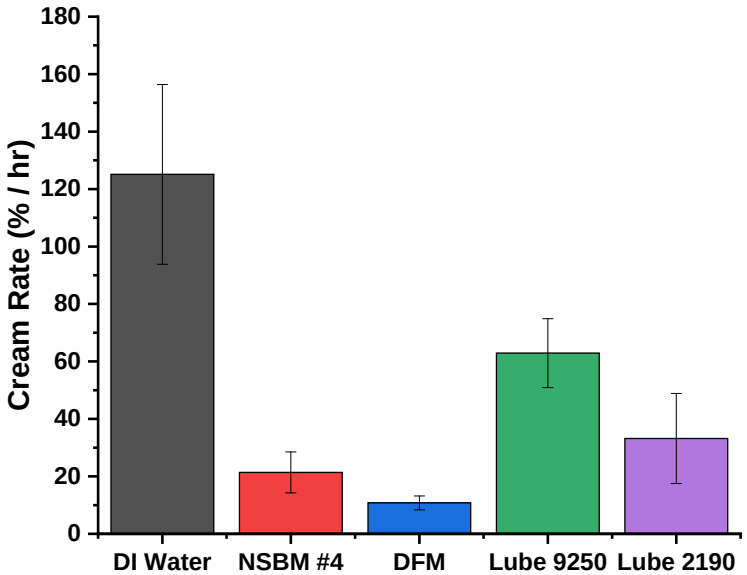
Salts and solids as well as increasing temperatures destabilize emulsions, while pH has little impact

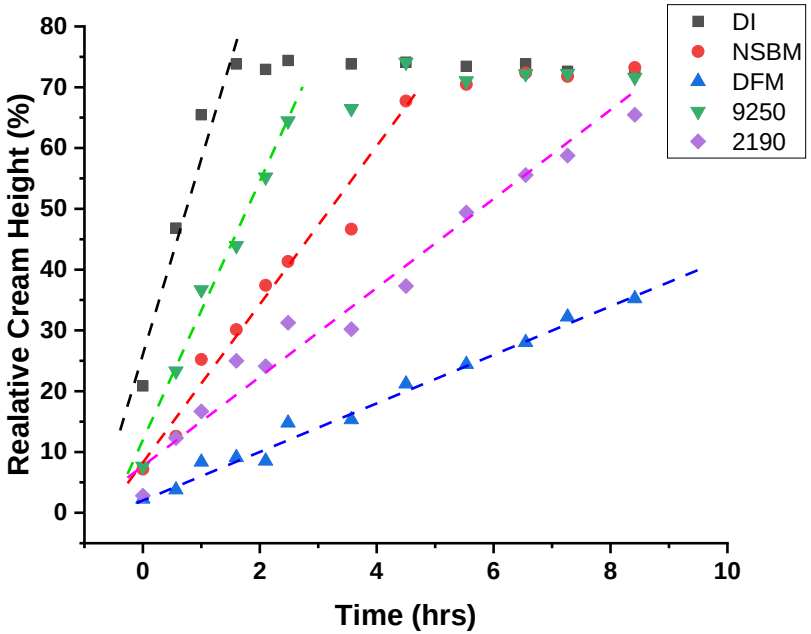
Impact of Fuel Additives on Emulsion Stability

- Motivation
  - Explore transport of additives from oil/fuel phase to aqueous phase of a bilgewater system
  - Determine impacts that these additives have on water quality and emulsion stability
- Approach
  - Model Bilgewater Fuels and Oils were exposed to deionized (DI) water for 24 hrs
  - DI water was extracted and used for water quality analysis and emulsion stability testing
- Analysis
  - Visual observations
  - Creaming rate

Experimental set up for extracting water miscible components from bilgewater oils

Impact of Fuel Additives on Emulsion Stability





Note: *DFM = Diesel Fuel, Marine*

Conclusions

- Cleaners on ships vary in composition and chemical properties
  - Bilgewater emulsion stability prediction challenging
- CMC could be used to evaluate a cleaner's likelihood of emulsifying oil
- Bilgewater emulsion stability is impacted by:
  - Environmental
    - Salinity
    - Temperature
  - Fuel additives

Future Work

- Continue investigating impact of hydrocarbon phase on emulsion formation and stabilization
- Develop model using advanced algorithm techniques
  - Current testing uses classification and regression models
- Apply knowledge gained to tangential research areas
  - Aqueous film forming foam behavior

Benefits to DoD

- More refined bilge management practices
  - Alter treatment system operational profiles based on shipboard activities
- Improved selection of appropriate bilgewater treatment technologies
  - Assess type of treatment system required based on the cleaners procured and typical shipboard activities
- More informed bilge cleaner selection
  - Reduce or remove highly emulsifying cleaners from shipboard approved use lists

Acknowledgments

- Dr. Jared Church (Naval Surface Warfare Center, Carderock Division)
  - Expertise in Navy bilgewater characterization and treatment using chemical, electrochemical, and physical methods and micro and macro scale characterization techniques
- Dr. Woo Hyoung Lee and Ms. Daniela Diaz (University of Central Florida, Department of Civil, Environmental and Construction Engineering)
  - Expertise in solution characterization including development of novel microsensors, interfacial tension measurements, and colloid imaging
- Dr. Jeffrey Lundin (Naval Research Laboratory, Chemistry Division)
  - Expertise in solution characterization and chemical analysis including differential scanning calorimetry (DSC), zeta potential and emulsion size distribution, nuclear magnetic resonance (NMR) spectroscopy, and liquid chromatography-mass spectroscopy (LC-MS)

For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Waste-Reduction-and-Treatment-in-DoD-Operations/WP18-1114

Speaker Contact Information

danielle.paynter@navy.mil; 301-227-5089

SERDP DOD • EPA • DOE | ESTCP

Q&A Session 2

SERDP DOD • EPA • DOE | ESTCP

The next webinar is on June 18, 2020

Advances in the Treatment of 1,4-Dioxane in Mixed Contaminant Plumes

SERDP DOD • EPA • DOE | ESTCP

Survey Reminder

Please take a moment to complete the survey that will pop up on your screen when the webinar ends

SERDP DOD • EPA • DOE | ESTCP