**14th Annual OSC Readiness Training Program**

# 2011 OSC Readiness Training

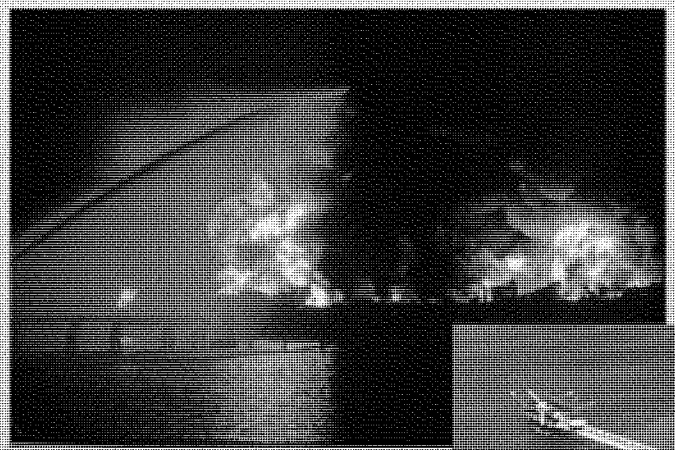
NCP Product Schedule / Selection Guide for Oil Spill Response Technologies / Alternative Response Tool Evaluation System for Oil Spill Response (ARTES)

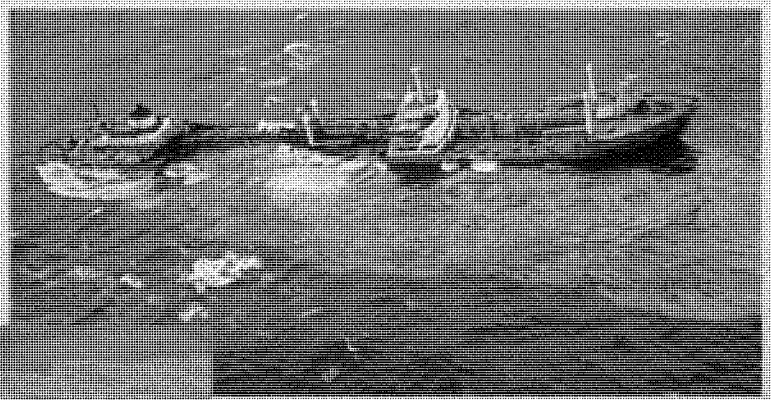
Training by OSCs for OSCs

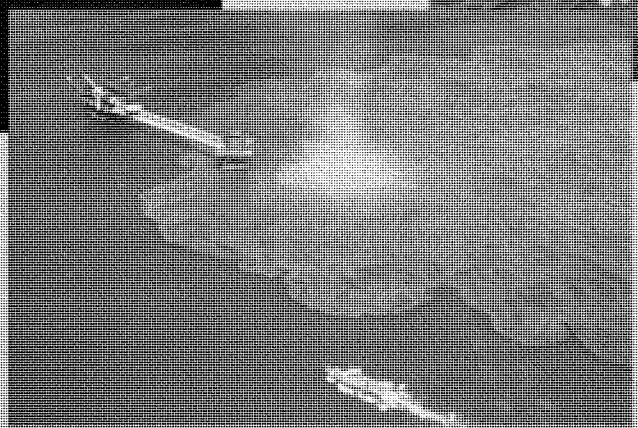
**January 31 – February 4, 2011**
**Orlando, Florida**
**www.oscreadiness.org**

# History and Background

- Past spill experiences shapes our current decision-making about countermeasures e.g., *Torrey Canyon*, *Ixtoc I* blowout, *Exxon Valdez, etc.*











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# History, Cont.d

- Use of "non-traditional" response technologies (e.g., early dispersants) ⇒ perceived damages
- Their use resulted in changes in Federal regulations:
  - National Contingency Plan, and
  - the Oil Pollution Act of 1990





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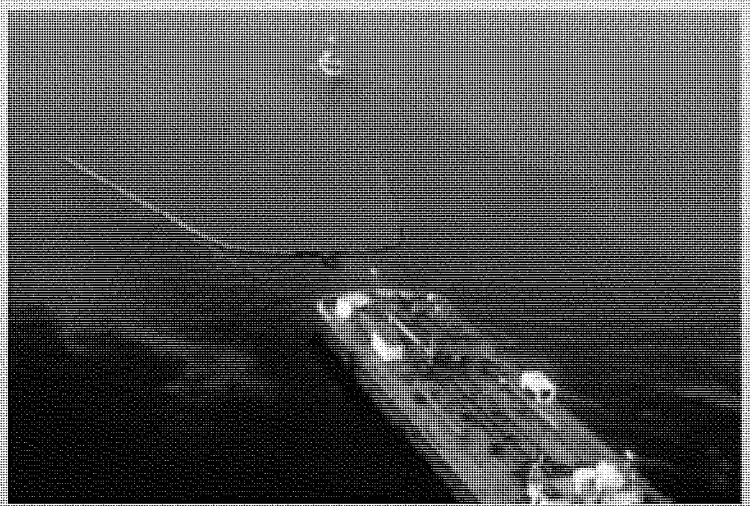
# High Comfort Level

- Traditional countermeasures (boom, skimmer, sorbents etc.) are a known entity



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# Oil Spill Technologies, Defined

- a.k.a. – "non-traditional" regulated countermeasures
- Countermeasures that are infrequently used; limited experience / knowledge about when these countermeasures could be useful and environmentally beneficial



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# Oil Spill Technologies, Defined

- Includes:
  - Dispersants
  - Bioremediation Agents
  - Surface Washing Agents
  - Shoreline Pre-treatment Agents
  - Surface Collecting Agents
  - Solidifiers
  - Elasticity Modifiers
  - Emulsion Treating Agents
  - Other Miscellaneous Agents



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# Discomfort with Oil Spill Technologies

- Decision-maker's wary of non-traditional response technologies

# Why?

- Lack of experience with the various products / strategies
- Perceived problems with their use:
  - Regulatory agency understanding?
  - Liability?
  - Result in additional environmental damage?
  - Lack of experienced application / recovery personnel
  - Difficult to interpret product information?
  - Vendors





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# Technologies Today

- Chemical products significantly changed fro past formulations; research now current and extensive on many products
- Standardized effectiveness and toxicity testing required
- Must be registered with EPA for use on oil spills in the US





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# Approach For Evaluating Technologies

- "Tools" available to response decision-makers:
  - The National Contingency Plan (NCP) Product Schedule (Subpart J - 40 CFR Part 300.900)
  - Selection Guide for Oil Spill Response Technologies
  - Applied Response Tool Evaluation System (ARTES)





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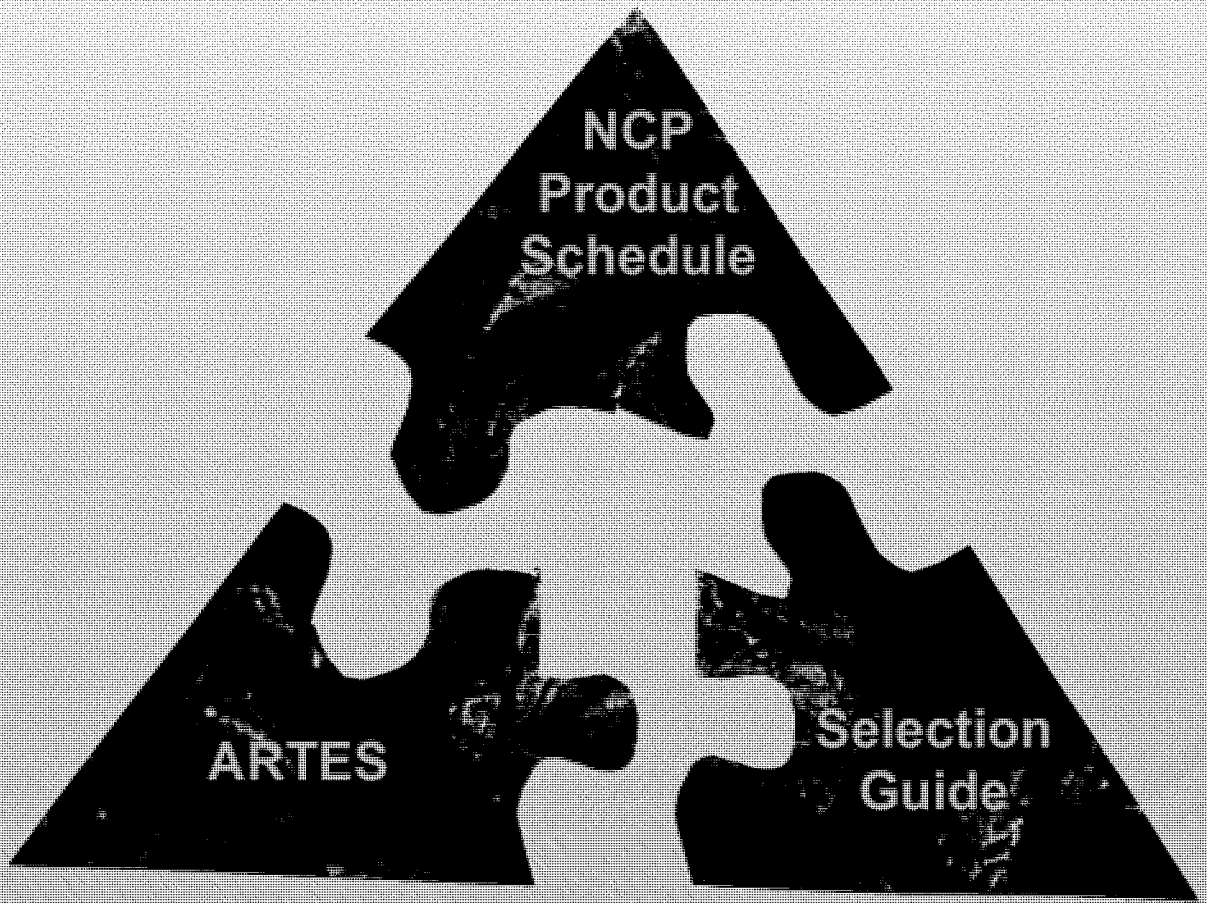
# Putting the Pieces Together for Response Decision-making

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# NCP Product Schedule

- Functions as the regulatory vehicle for use of any applied technologies
- Regulated under:
  - Section 311(d)(2) of the Clean Water Act, and
  - Section 4201 (a) of the Oil Pollution Act of 1990



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**Listing of a product does NOT mean that the product is recommended or endorsed by the USEPA for use on an oil spill;**

**Only that product has met minimum information requirements for listing.**

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# Product Categories on NCP PS

- Dispersants
- Surface Washing Agents
- Surface Collecting Agents
- Bioremediation Agents
- Miscellaneous Oil Spill Control Agents





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# Limitations of NCP PS

- Not designed for incident-specific decision-making
- Does not allow easy comparison of products
- No way to capture lessons learned for individual product use
- Limited to chemical and biological additive products, that is…not new or advanced mechanical strategies or techniques



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# Alternative Response Tool Evaluation System (ARTES)

- Focus of another presentation…
- Used to:
  - evaluate a product's appropriateness for use during a specific incident, under specific circumstances.
  - as a pre-evaluation to identify conditions under which favorable outcomes are anticipated when a product is used.





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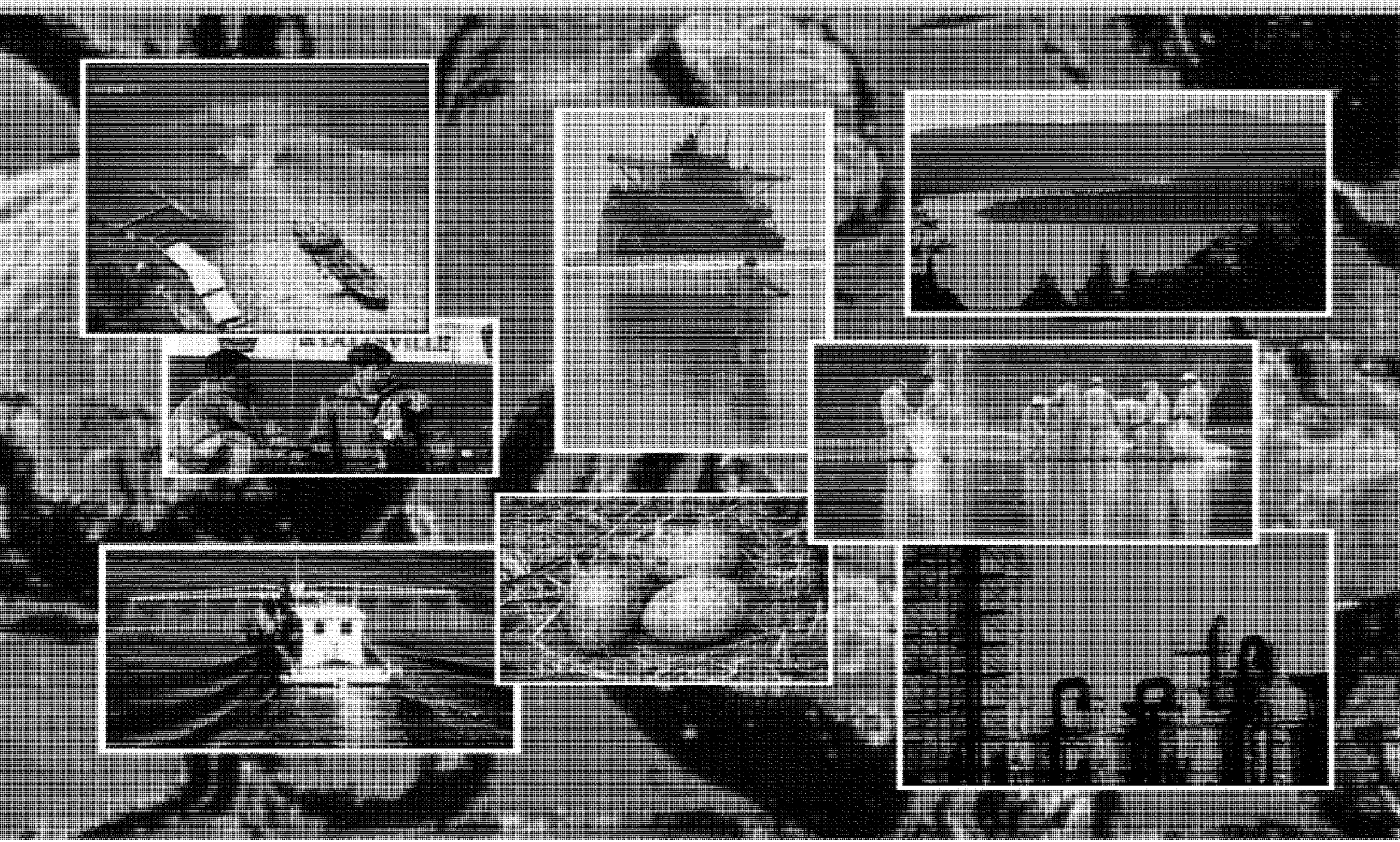
# Selection Guide for Oil Spill Response Countermeasures



# Why Selection Guide Developed

- Designed to provide OSCs and other response decision-makers with an easy-to-use technical guidance database for considering applied oil spill technologies for use during an incident.
- Developed by Region III in cooperation with Region IV





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# Selection Guide, Cont'd

- Two volumes:
  - Decision-making information (Nationally applicable) and
  - Implementation/operational support documentation (regionally customizable)
- Provides information requested by decision-makers to consider, select, and implement an environmentally-appropriate product or technology





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# Selection Guide Information

- Bioremediation Agents
- Dispersants
- Elasticity Modifiers
- Emulsion Treating Agents
- *In situ* Burning on Land
- *In situ* Burning on Water
- Shoreline Pre-treatment Agents
- Solidifiers
- Sorbents
- Surface Collecting Agents
- Surface Washing Agents

***Different Categories than the NCP!***





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# Information, Cont'd

- Information Categories
  - Mechanism of Action
  - When to Use
  - Authority Required
  - Availability
  - General Application Requirements
  - Health and Safety Concerns
  - Limiting Factors/ Best Management Practices
  - Monitoring Requirements / Suggestions
  - Waste Generation and Disposal Issues
  - References



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# Content

- Instructions and matrices for selecting a strategy or countermeasure using job aid techniques
- Allows direct product comparisons among products and categories/strategies using product comparison tables
- Establishes the need for monitoring and capturing lessons learned





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# Content, Cont'd

- Glossary used with various products/ strategies
- History and status of product use (case study examples)
- Toxicity primer – how toxicity is measured and what the numbers really mean





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# Strengths of Selection Guide

- Allows comparison of similar products as well as comparison of various strategies to determine the best response
- Developed using "job aid" techniques
- Allows documentation for the decision-making process





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# Strengths, Cont'd

- Provides situation–specific assistance in the selection of products and strategies during planning and response, including new products / strategies
- Provides guidance on the use of response technologies and products
- Developed to capture and incorporate lessons learned





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# Limitations of Selection Guide

- Only as good as the information submitted; data could be limited
- Should be updated as new information becomes available (e.g., ARTES evaluations, actual use)
- June 2009 Edition available in:
  - paper format,
  - internet download (January 2003) from www.response.restoration.noaa.gov/oilaids.html
  - interactive e-version (to be released soon)





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# Limitations, Cont'd

- Decision-makers need to ensure that they are making their decisions with the most current information available
- Not a cook book! – Still have to evaluate incident-specific information with product(s) in mind
- Need Evaluation Team (OSC, SSC, State, USFWS, etc.) to assist with review to ensure effective evaluation for incident-specific conditions for FOSC.





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# e-version of the Guide

- e-version of the Selection Guide finalized
  - Components & use focus of training after lunch
  - Hands-on practical use of the guide
    - Example scenarios will be used to work through the Selection Guide Process
    - Input your own scenarios





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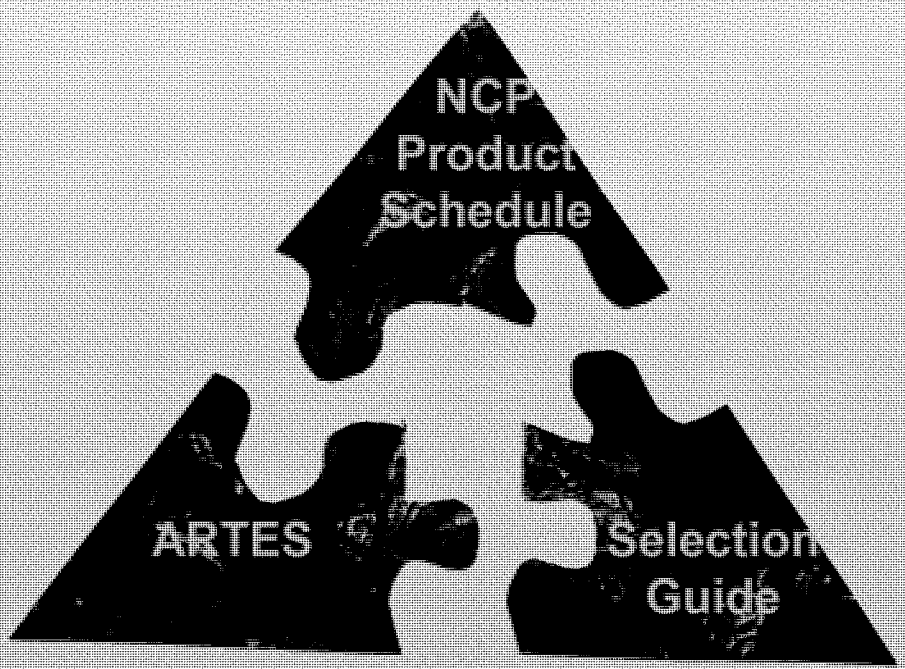
# In Summary

- Use all the pieces to solve the puzzle (make a decision)





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# In Summary, Cont'd

- Most effective use of these tools is in a coordinated manner
- NCP is the first step and requirement; provides guiding legislation; Nationally applicable information
- ARTES assists in the evaluation of single product / technology for regional or incident-specific conditions





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# In Summary, Cont'd

- Selection Guide allows:
  - Screening the incident for possible strategies/ products that could add value to a response, and
  - Comparison of products / strategies of interest relative to other techniques to select the most appropriate technology





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# Thanks for your attention!

If you have any questions, please call
Debbie Scholz
843-367-5126

# 14th Annual OSC Readiness Training Program

# OSC Training-Orlando, FL-2010
# Alternative Countermeasures

Presenter: Albert D. Venosa, Ph.D.
U.S. EPA-ORD
Director, Land Remediation & Pollution Control Div.
National Risk Management Research Laboratory
Cincinnati, OH 45268
Date: February 3, 2010

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www.oscreadiness.org

# Outline of Presentation

- Two technologies to be discussed
  - Bioremediation
    - Definitions
    - Overview
    - The Process
  - Dispersants
    - Factors needed for effectiveness
    - Wave tank studies
  - Spill scenarios





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# BIOREMEDIATION

# What is bioremediation?

- The exploitation of living microorganisms to convert organic contaminants into biomass and innocuous end products
  - Innocuous end products include $CO_2$, water, and incompletely oxidized organics





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# How Biological Clean-up Is Achieved

- Naturally, without human intervention
  - Called "Natural Attenuation (NA)" or "Monitored Natural Attenuation (MNA)"
- Accelerated (requires human intervention)
  - Bioaugmentation
  - Biostimulation





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# Natural Attenuation

- The disappearance of oil via natural means, including:
  - Volatilization
  - Washout
  - Biodegradation
  - Photolysis



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# Basics of Biological Treatment





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# Composition of Living Matter

- Among other trace substances, the primary components are:
  - Carbon: basic structural component of protoplasm and biomolecules
  - Nitrogen: used in formation of amino acids for protein synthesis
  - Phosphorus: used in formation of genetic material, high energy bonds, and membranes





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# What are hydrocarbons?

- Organic compounds containing carbon and hydrogen
  - May contain fully saturated bonds (no double bonds) (alkanes)
  - May contain some unsaturated bonds (double bonds) (alkenes)
  - May be linear or cyclic and saturated (cyclohexane, hopane)
  - May be aromatic with single or fused rings (benzene, phenanthrene)
- When oil is spilled into the environment, it becomes food for living microorganisms able to utilize it for growth





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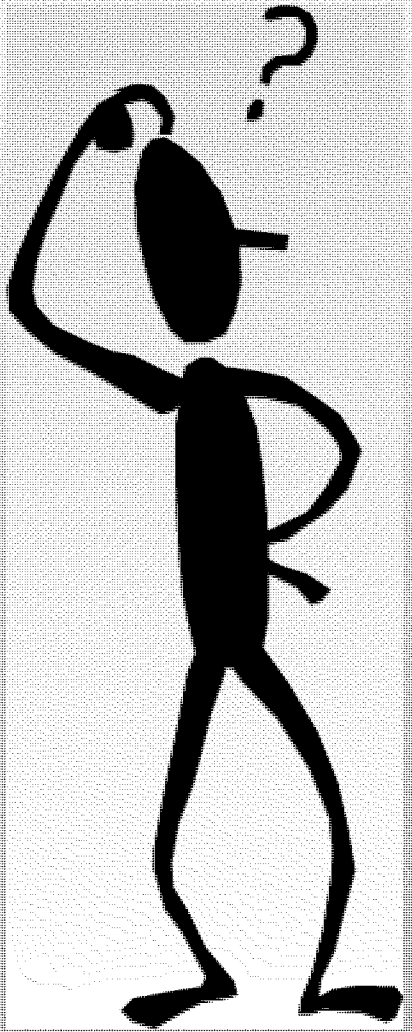
# What is the goal of a microorganism?







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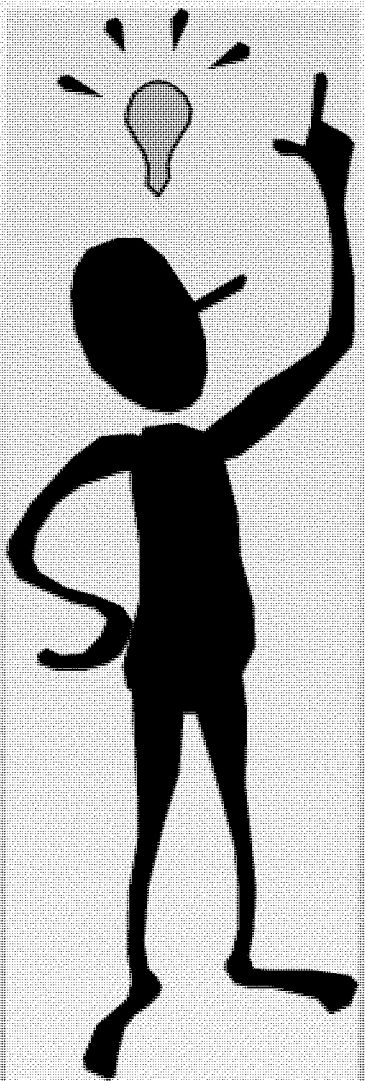
# To make another microorganism!







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# Process of Biodegradation

- Converting food into biomass requires several steps
  - 1st step is addition of OH-group to alkane or PAH ring forming an **alcohol** (R-OH)
  - Progressive **oxidation** to aldehyde (R-CHO), then to acid (R-COOH) leading to chain length reduction
  - As oxygen added to hydrocarbons, compounds become more polar, more water soluble
  - Polar compounds less toxic, more biodegradable
  - In case of PAH, **ring fission** occurs followed by chain length reduction as above
- Eventually to water, $CO_2$, biomass, and innocuous end products





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# Biodegradable Components of Petroleum Oils

- Alkanes (saturates): easy
- Polycyclic Aromatic Hydrocarbons (PAHs): moderate
  - Fused aromatic rings, must be split
  - Biodegradability depends on number of rings and alkyl substituted groups
- Heavy polar compounds (NSO): difficult
- Asphaltenes: very difficult, complex

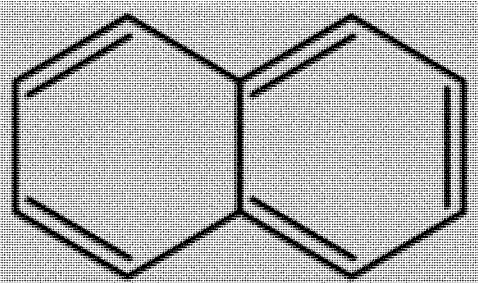
# Examples

- Straight Chain Alkanes: easy to degrade. Example: HEPTADECANE (17 carbons)

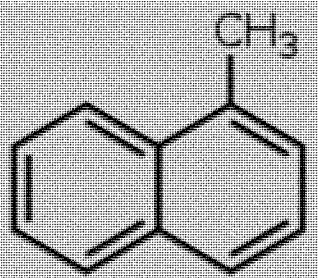
- Branched alkanes: harder to degrade. Example: PRISTANE (19 carbons)

- PAHs

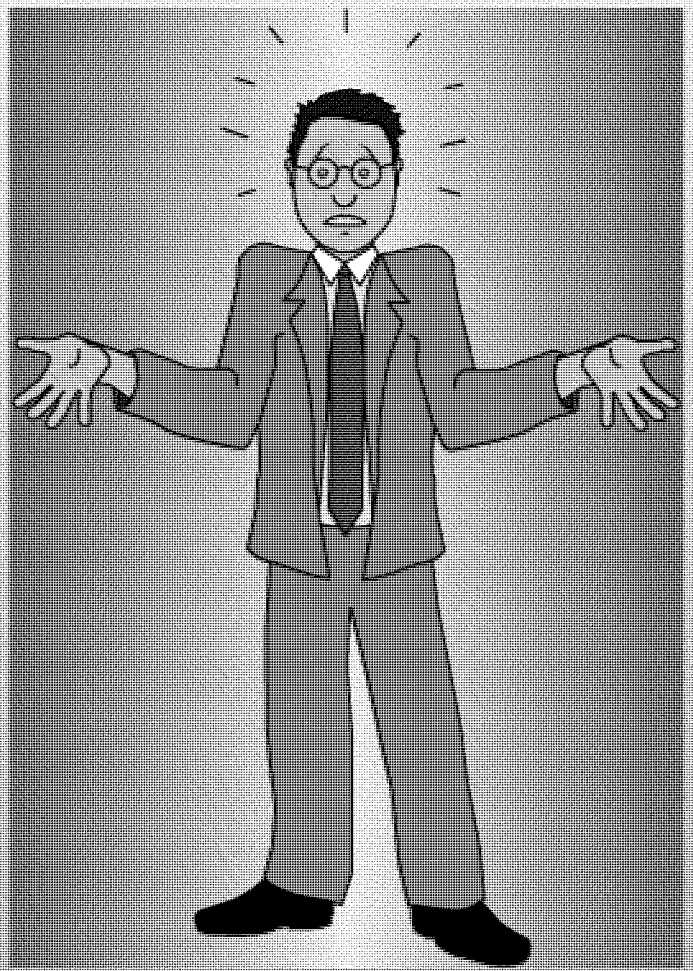
(parent, easier)



(alkyl-substituted, harder)



# What are the requirements for successful bioremediation?







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# Requirements for Success

- Bacteria with metabolic capabilities must be present
- Rates of growth can be maximized by ensuring that:
  - Adequate supplies of oxygen and nutrients must be present
  - pH between 6 and 9
  - No other adverse circumstances
    - High salt content
    - Low moisture
- Weight of oil affects success (lighter oils more biodegradable, asphaltenes tend to inhibit diffusion)
- Oil surface area important because biodegradation occurs at oil-water or oil-sediment interface





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# Where are oil degraders found?

- Hydrocarbons are found everywhere
- Hydrocarbon degraders are found everywhere





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# An oil spill causes huge influx of carbon (food). How does an organism cope?

- To convert carbon to biomass, bacteria must have nitrogen and phosphorus and oxygen
- Bacteria will grow slowly in presence of usual amounts of N and P in nature
- To maximize rate, give more N and P
- May need to provide oxygen





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# Bioremediation Approaches

- Bioaugmentation
  - The addition of highly competent microbial cultures to an impacted site to accelerate or kick-start the biodegradation process.
- Biostimulation
  - The addition of factors (usually nutrients) that limit the ability of the degrading populations to grow at their maximum rate.





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# Assumptions for Successful Bioaugmentation

- Culture must be able to grow rapidly on oil
  - Can be determined in lab (NCP product testing)
- Culture must be able to colonize the environment rapidly and out-compete the natural communities
  - Very difficult to accomplish





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# Quiz Question:

Based on what you know so far, do you think adding a living culture to a spill site will accomplish the cleanup goal?

Why or why not?





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# Answer

- No need to add cultures to an oil spill
- Bacteria need what is lacking: N and P, and if the environment is anaerobic, also need oxygen
- We have 2 guidance documents that describe how to calculate and add nutrients to an oil spill site
  - Available on EPA website:

http://www.epa.gov/emergencies/publications.htm#bio





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# Wetland Environments

- Oil spills very likely to affect coastal marshes and wetlands
- Most research data available are ORD-funded studies in Quebec and Nova Scotia





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# Properties of Wetland Environments

- Usually oxygen limited, very quiescent (little wave action)
  - Become anaerobic a few mm below ground surface
- Likely not nutrient-limited
  - However, plants easily out-compete bacteria for available nutrients





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# How is bioremediation applied to wetlands?

- Depends on goal:
  - If oil removal is main goal, natural attenuation may be the favored strategy, especially if penetration took place
    - Biostimulation might still be appropriate if significant penetration has not occurred
  - If ecosystem recovery is main goal, nutrient addition may speed restoration substantially





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# Plot Recovery in St. Lawrence River Study, Mid-Summer

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# Plot Recovery, St. Lawrence River, end of summer

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# Plot Recovery, St. Lawrence River, 2nd year

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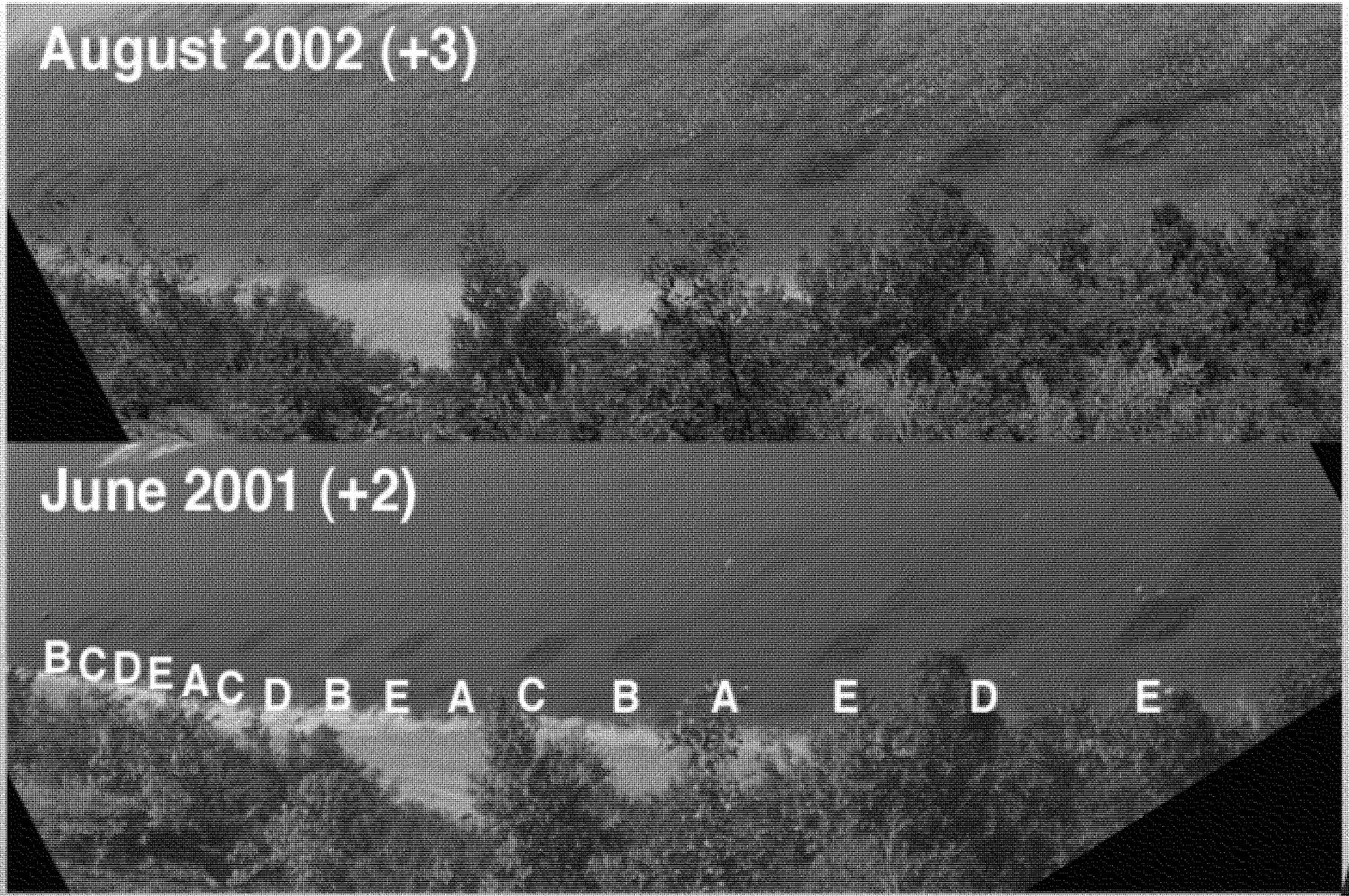




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# Land Bioremediation

# Properties of Terrestrial Environments

- Lateral spread of oil less widespread than in coastal wetlands or beaches
- Ecological damage typically localized and limited
- Problem: vertical movement to water table





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# Land Farming

- Same principles apply:
  - Maintenance of supply of nutrients
  - Maintain aerobic conditions
    - At shallow depths, tilling
    - At deeper depths, bioventing or excavation followed by *ex-situ* techniques like biopiles or composting
  - Fertilizer needs for land treatment
    - Typically, ratio of 100C:10N:1P used (minimize use of nitrate)
    - Prefer adding in several increments, not all at once





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# Factors Affecting Land Treatment

- pH control neutral to slightly alkaline (6.5 to 8.5)
- Moisture important
- Nutrients
  - Without spill, microbial activity usually limited by carbon
  - After spill, N and P usually limiting





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# Vegetable Oil

- Properties similar to petroleum
  - Light nonaqueous-phase liquid (LNAPL)
- Coating of feathers, fur, and gills is harmful
  - Absence of odor and sheen results in reduced avoidance
  - Reduces thermal insulation and buoyancy
- May burn if ignited
- May clog water treatment plants (due to the polymerization property)
- Surface oil may prevent re-aeration of water column





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# Composition of Vegetable Oils

- Triglycerides
  - Long chain fatty acids coupled to glycerol, a 3-carbon compound with 3 alcohol (-OH) groups
  - Fatty acids are long chain alkanes (saturated) or alkenes (unsaturated) with a carboxylic acid group at end (-COOH)
    - To make a triglyceride, the fatty acids replace the –OH groups
  - Examples
    - Stearic acid (18 carbons with no double bonds)
    - Oleic acid (18 carbons with one double bond)
    - Linoleic acid (18 carbons with two double bonds)
    - Linolenic acid (18 carbons with three double bonds)





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# Chemical Effects of Vegetable Oil Spills

- High BOD may cause oxygen depletion
  - Greater effect on DO than petroleum oils
- Unsaturated oils (liquids at cold temperatures) are subject to chemical (abiotic) oxidation
  - Polymerization due to chemical oxidation and cross-linking
  - Rancid odors may develop rapidly
  - Unsaturated oils form gum balls and varnishes
- Saturated oils turn solid at cool temperatures
- May be toxic or form toxic products
  - Especially free fatty acids and chemical oxidation products





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# Biodegradability of Vegetable Oils

- Degradable both aerobically and anaerobically
  - Because they're already oxygenated (fatty acids), anaerobic biodegradation can proceed rapidly
  - This distinguishes these oils from petroleum oils
- If polymerization occurs, biodegradation is inhibited
  - Gumball and varnish formation





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# DISPERSANTS

# What are dispersants?

- Compounds that contain one or more surface active agents (surfactants) and possibly a solvent
  - Surfactants reduce the oil-water interfacial tension
  - Solvents reduce oil viscosity
- When applied to a slick, small droplets are formed that intermix in the water column, increasing the surface area of the oil





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# What makes dispersants effective?

- Properties of the oil
  - Viscosity
  - Weight
- Slick thickness
- Dispersant:oil ratio (DOR), best at 1:25 to 1:50
- Surfactant loss at the water surface
- Surface tension of water
- Salinity
- Mixing energy due to wave action





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# Importance of Mixing Energy

- Dispersion takes place at small scale (< 1 cm)
  - Simulation in lab possible since small eddies similar to eddies at sea
  - Energy dissipation rate per unit mass is the measure of mixing energy
    - Units are Watts/kg water
    - Dissipation of kinetic energy due to laminar and turbulent shears, which are directly proportional to velocity gradients
    - Measure velocity gradients to compute energy dissipation rate





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# Wave Tank at Halifax, NS

- A collaboration between EPA and Fisheries & Oceans Canada (DFO)
- Wave tank fabricated at the Bedford Institute of Oceanography (BIO), Dartmouth, NS
- Objective: to study dispersant effectiveness at various mixing energies representative of sea states
  - Experiments have taken place to define energy of breaking and non-breaking waves
  - Batch and flow-through conditions





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# Characteristics of Wave Tank

- Dimensions: 32 m x 2 m x 0.6 m
- Materials of construction: epoxy-coated steel
- Computer-controlled wave maker able to produce regular and breaking waves
- Wave absorbers to mitigate reflection
- Can be drained and filled in < 2 h
  - Allows for cleaning between runs to prevent residuals from confounding experiments
- Can be operated in batch and flow-through modes





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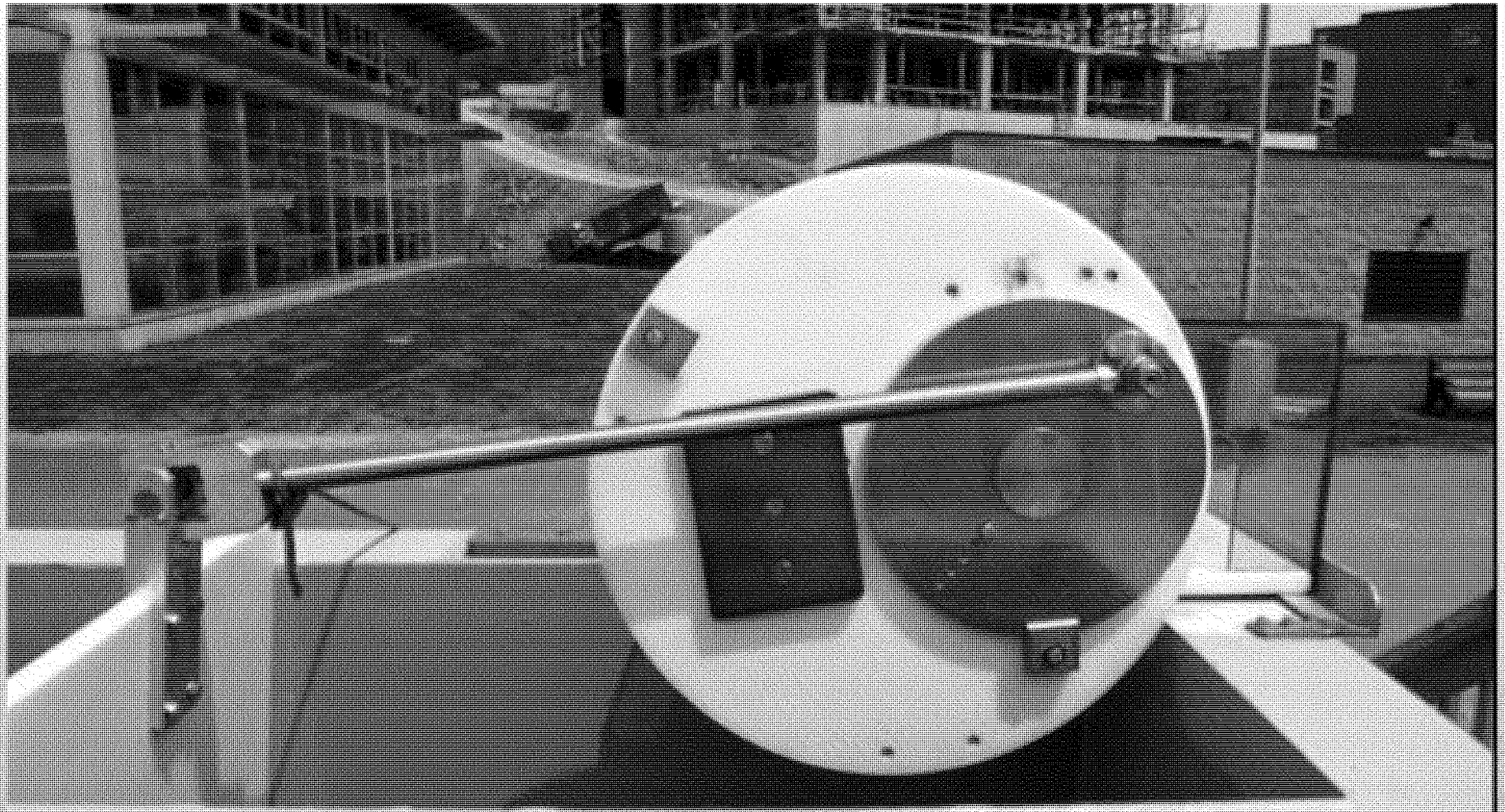

Wave Maker

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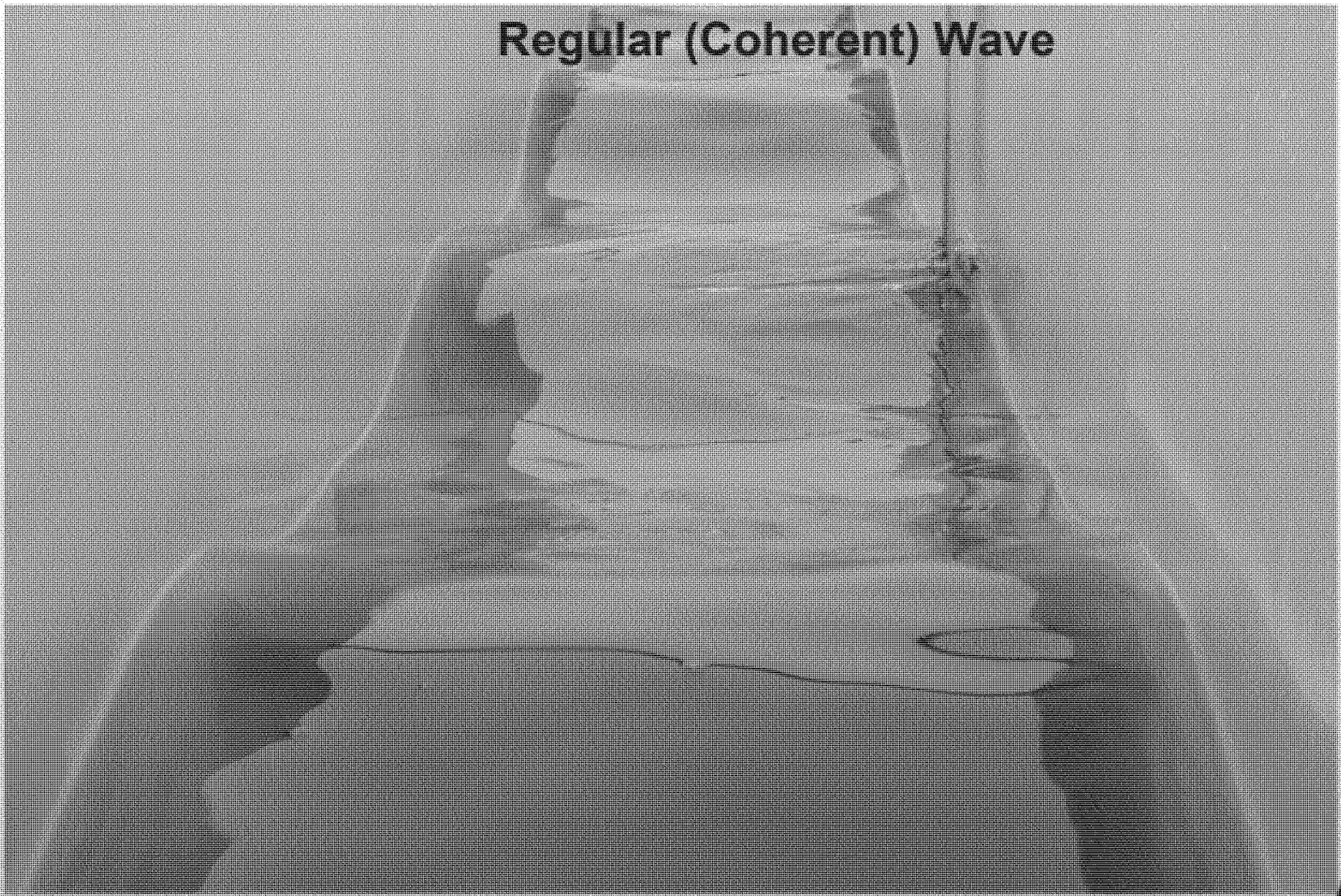
# Regular (Coherent) Wave





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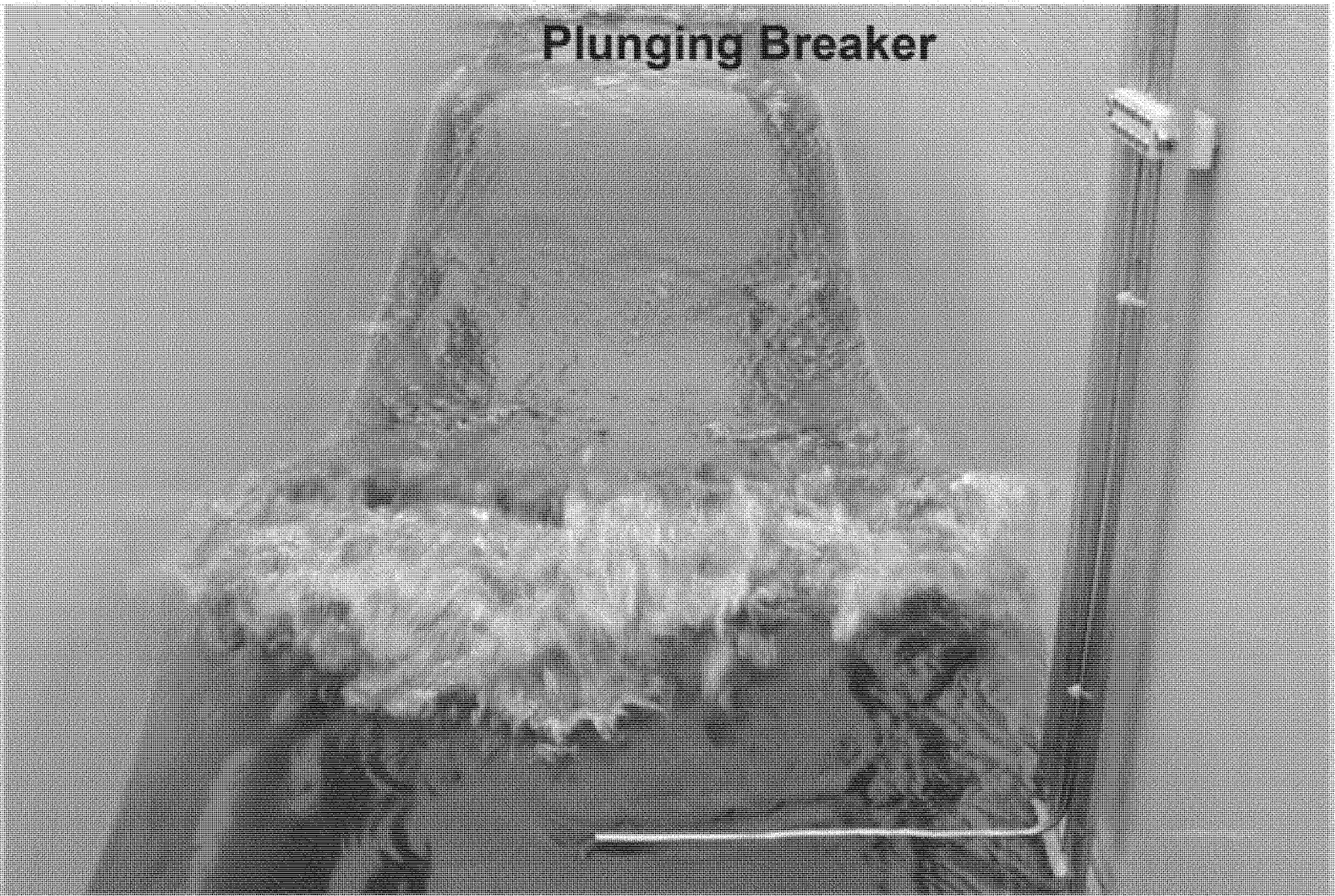
# Mild, Spilling Breaker


Plunging Breaker

# Dispersant Effectiveness

- Breaking waves are important for effective and lasting dispersion
  - Breaking waves shear oil slick into tiny droplets that don't easily recoalesce
  - Breakers push oil downwards into water column where currents may carry the dispersed oil away
- Regular waves disperse oil somewhat but do not impart sufficient energy to break up the oil into small droplets or push the droplets down deeply into the water column
  - They do maintain sufficient energy to maintain dispersed state
- Mineral fines enhance dispersion of oil into water column





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# Summary of Dispersant Use in Gulf Spill

- EPA science team developed sampling and monitoring plan for deep sea injection and surface application
- Called for measurement of:
  - Dispersed oil by fluorometric techniques
    - CDOM (colored dissolved organic matter)
    - CTD (conductivity, temperature, depth)
    - More advanced but proven techniques (fixed wavelength)
  - Droplet size distribution (LISST)
  - Analytical chemistry (GC/MS and TPH) of batch samples
  - Dissolved oxygen
    - Hypoxic level was 2 mg/L (or 1.4 mL/L)
  - Toxicity by rotifer assay (Rototox)





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# Subsurface Injection of Dispersant

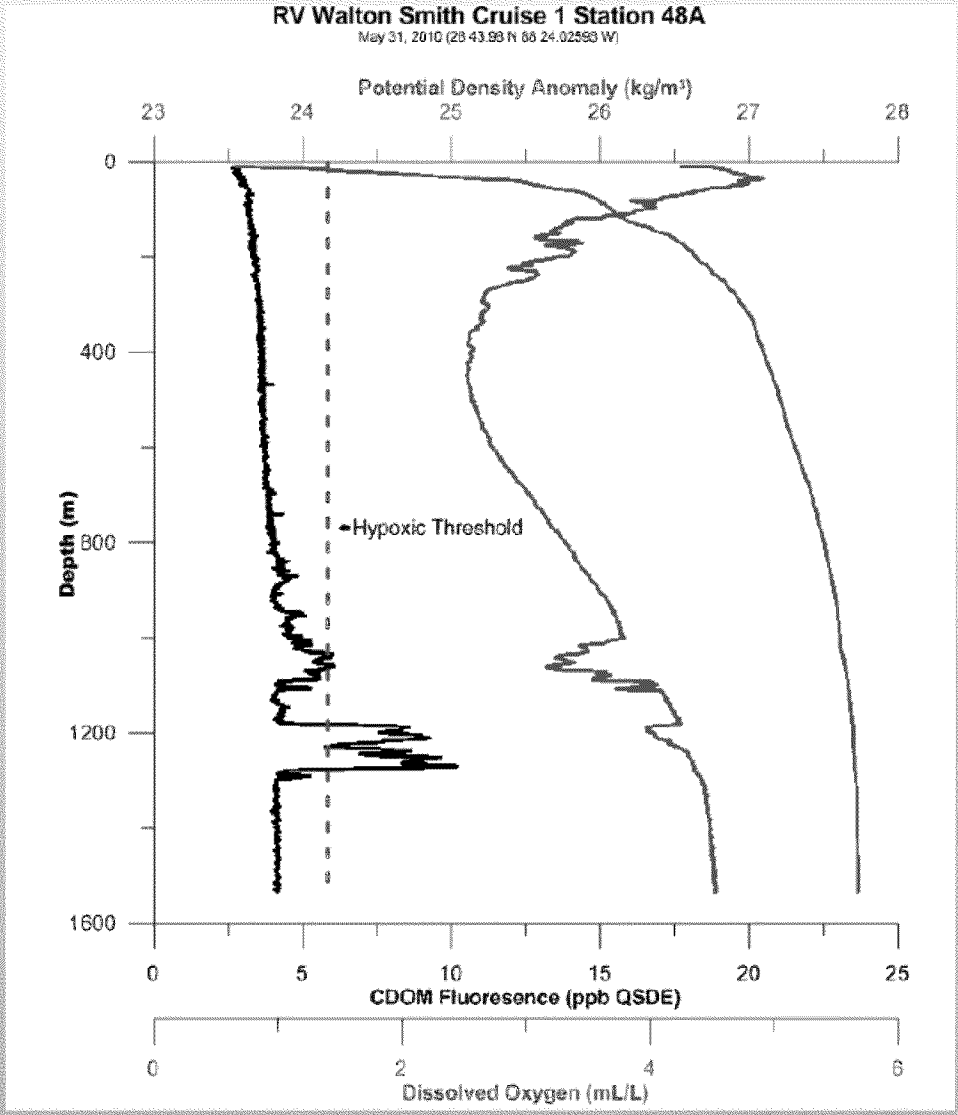
- Volume based on DOR, high degree of uncertainty
  - Optimum volumetric DOR ~ 1:25 to 1:50
  - Flow rate of oil unknown for first 30 days
    - Originally thought to be 5,000 bbl/d (210,000 gpd)—gave a DOR of 1:14 (too much dispersant)
    - Later adjusted higher and higher to final flow of 62,000 bbl/d (2.6 million gpd or a DOR of 1:174 (too little dispersant)
    - Due to uncertainty of ecological effects, dispersant use was fixed at 15,000 gpd for spill duration
- Dispersed oil plume detected consistently at 1,100-1,300 m
  - Moving predominantly in SW and NE directions (isobath flow)
  - Active natural seeps mapped at 12 SW and 17 km NE of wellhead





ED_001324_00007269-00051

# Vertical profile showing 2 DO depressions coincident with fluorescence peaks



# Future Research Based on BP Spill

- Improvements in fluorometric monitoring of dispersed and non-dispersed oil plumes needed
  - Questions remain on optimum sensor configuration and NOM interference
  - 4-D mapping of dispersed oil plumes (leverage with NOAA)
  - Improved, innovative laser-based fluorometry (leverage with Canada DFO)
  - Better, faster analytical methods for measuring fate and transport of dispersed oil
- Develop green oil spill mitigation approaches for reduced toxicity and persistence in environment
- Better understanding of water-in-oil emulsions (mousse)
- Assessment of weathering effects on dispersion of oil
- Biodegradability of tar balls and other emulsions
- Exposure assessment scenarios for human and ecosystem effects
- Toxicity testing over many trophic levels
- Development of comparative risk assessments for sensitive species to inform risk management options





ED_001324_00007269-00053

# Application of SMART Protocol OSC Readiness, 2011

Harry L. Allen
US EPA/ERT

# What is SMART?

(From the NOAA Dispersant Applicator's Observation Job Aid)

- "Special Monitoring of Applied Response Technologies" (SMART) as a joint product of the USCG, NOAA, and EPA.
- SMART grew out of the Special Response Operational Monitoring Plan (SROMP) to avoid arguments over whether or not the dispersants were working.
- SMART: establishes a monitoring system for rapid collection and reporting of real-time, scientifically based information, in order to assist the Unified Command with decision-making during in situ burning or dispersant operations.
- SMART recommends monitoring methods, equipment, personnel training, and procedures that strike a balance between the operational demand for rapid response and the Unified Command's need for feedback from the field in order to make informed decisions.

# How do we use SMART?

- SMART applies particularly to the use of chemical dispersants and *in situ* burning as response alternatives.
- SMART is a decision-making tool during spill operations at a response and a planning tool where pre-approval is sought for burning or dispersant use.
- The SMART protocol has been updated and is available on the NOAA Website:
- http://response.restoration.noaa.gov
- Differences between NOAA and EPA arise over the interpretation of “response technology effectiveness.”

# How much dispersion is “effective” and will it cause aquatic toxicity?

- The NCP Product Schedule lists the effectiveness and toxicity of chemical countermeasures, but the RRT needs to approve their use.
- The minimum requirements for listing are dispersant effectiveness of 45% at the application rate of 1:20 Dispersant to Oil Ratio (DOR) in a swirling flask and a toxicity <1/10 LC50. The next slides are typical examples.
- Researchers have demonstrated effective dispersion in the lab at DORs of 1:25 and 1:100 using the new baffled flask test.
- The actual rate for the Deep Sea dispersant application at the well-head was about 1:195 (9 gpm/1,650 gpm).

## SUMMARY OF SUBPART J NOTEBOOK INFORMATION ON DISPERSANT FORMULATIONS

| Material Tested | Species | LC50 (ppm) | |
|---|---|---|---|
| COREXIT® EC9500A | Menidia beryllina | 25.20 96-hr | |
| | Mysidopsis bahia | 32.23 48-hr | |
| No. 2 Fuel Oil | Menidia beryllina | 10.72 96-hr | |
| | Mysidopsis bahia | 16.12 48-hr | |
| COREXIT® EC9500A & | Menidia beryllina | 2.61 96-hr | |
| No. 2 Fuel Oil (1:10) | Mysidopsis bahia | 3.40 48-hr | More toxic when dispersed. |
| Reference Toxicant (SDS) | Menidia beryllina | 7.07 96-hr | |
| | Mysidopsis bahia | 9.82 48-hr | |

## SWIRLING FLASK DISPERSANT EFFECTIVENESS TEST FOR COREXIT 9500A TEST WITH SOUTH LOUISIANA (S/L) AND PRUDHOE BAY (P/B) CRUDE OILS

| Oil Effectiveness (%) | % |
|---|---|
| Prudhoe Bay Crude | 45.3% |
| South Louisiana Crude | 54.7% |
| Average of Prudhoe Bay and South Louisiana Crudes | 50.0% |

# Use SMART to know you are getting effective dispersion?

- SMART Tier 1 relies on visual observation of dispersant effectiveness by trained observers.
- SMART Tier 2 employs field analytical techniques such as fluorometry (referenced to background), turbidity, droplet size distribution, conductivity, temperature, and depth (CTD) to estimate dispersion.
- SMART Tier 3 requires sampling and analysis to determine what oil fractions are being dispersed, whether the emulsions are physical or chemical, and whether there are toxic chemicals in the emulsion. Lab work is usually required. Dissolved oxygen is also considered a Tier 3 analyte, but electronic DO meters need lab calibration.

# Estimating Initial Oil on the Water

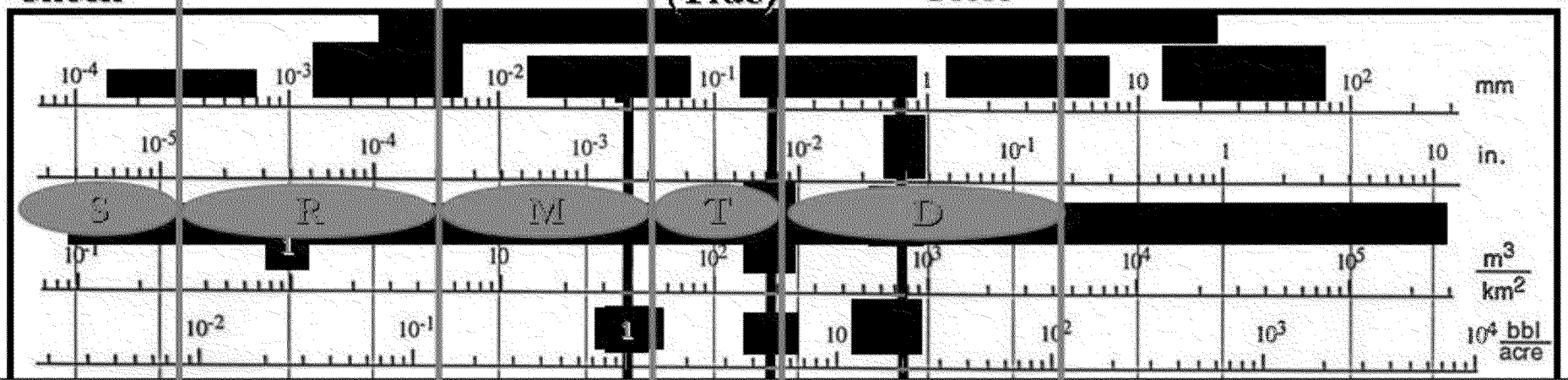
- It is an important first step to estimate the amount of oil on the surface in order to determine the required dispersant loading or to predict the feasibility of *in situ* burning.
- Al Allen of Spiltec has created an elegant oil thickness estimation system. Using this and an estimate of the area of oil coverage, we can calculate oil volume on the surface. If we have made an initial estimate before dispersant application, the relative degree of dispersion can be estimated as closely as by any other means.

# Visual Estimation of Oil Thickness & Quantity

Note:
1 μm = 1 $m^3/km^2$
≈ 0.026 bbl/acre

Color Code

| Silvery Grey Sheen | Rainbow | Metallic | Trans. Dark (True) | Dark (True) Color |
|---|---|---|---|---|
| 0.3 μm<br>$3 \times 10^{-4}$ mm<br>$1.2 \times 10^{-5}$ in. | 5 μm<br>$5 \times 10^{-3}$ mm<br>$2 \times 10^{-4}$ in. | 50 μm<br>$5 \times 10^{-2}$ mm<br>$2 \times 10^{-3}$ in. | 200 μm<br>$2 \times 10^{-1}$ mm<br>$8 \times 10^{-3}$ in. | 4,000 μm<br>4 mm<br>0.16 in. |




| 0.1 μm | 1 μm | 10 μm | 100 μm | 1000 μm |
|---|---|---|---|---|
| $10^{-4}$ mm | $10^{-3}$ mm | $10^{-2}$ mm | $10^{-1}$ mm | 1 mm |
| $4 \times 10^{-6}$ in. | $4 \times 10^{-5}$ in. | $4 \times 10^{-4}$ in. | $4 \times 10^{-3}$ in. | $4 \times 10^{-2}$ in. |

If not bounding, use as "nominal" mid-range values for each code #

Crude Oils Appear Dark ("True") in Color

Warm Stable

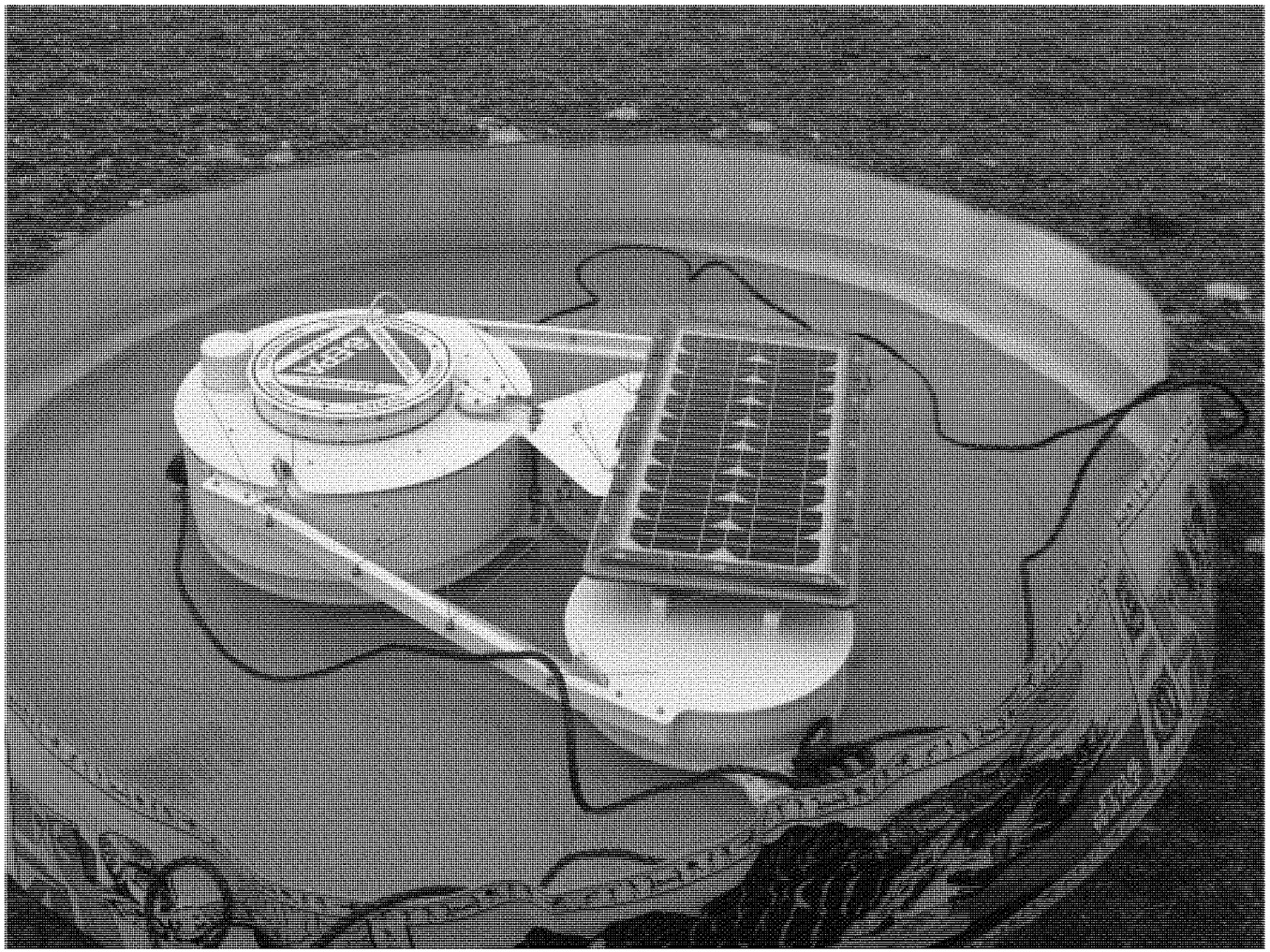
Emulsions

Cold Stable

Dr. Alan A. Allen, Spiltec

# The Leakwise Detector “Waverider” by GE Systems

May be used to measure the thickness of floating or emulsified oil remotely. Then it emails  and texts this information to Command.



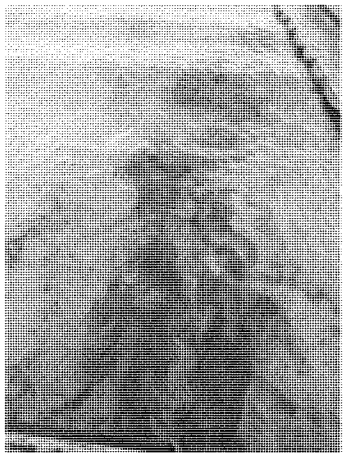
# Standardizing SMART Tier 1

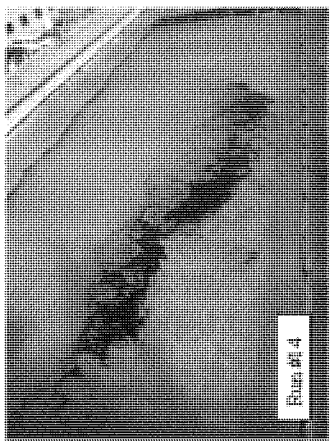
- Visual assessment of oil slick and oil in surface waters:
  - Trained observers may be hard to find.
  - Attempts to standardize observation and reporting of visual dispersion observations
  - Assesses ONLY initial break up of slick into dispersed oil droplets
  - Remember that dilution of the dispersant may allow the oil to resurface after a few hours. Think “Terminator 2.”

| Lewis Four Point Effectiveness Scale | |
|---|---|
| **Effectiveness rating** | **Description[a]** |
| 1 | No visible evidence of dispersion |
| 2 | Some evidence of partial dispersion |
| 3 | Moderate and incomplete dispersion |
| 4 | Rapid and complete dispersion |

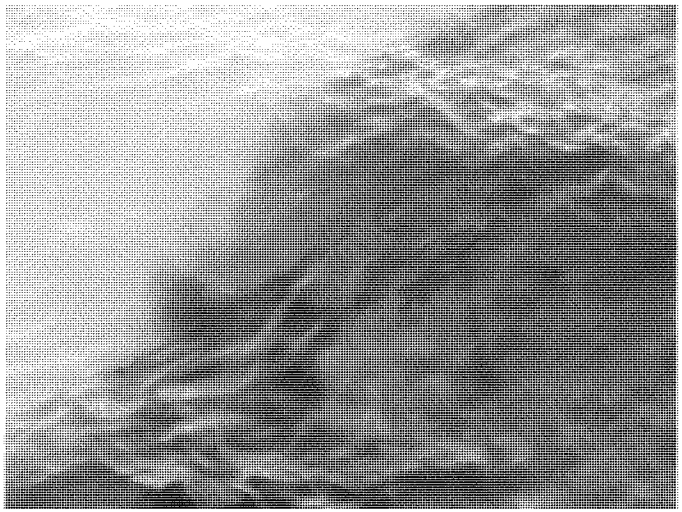
a. Based only on behavior of oil in first 15 minutes after dispersant added and agitated by waves.

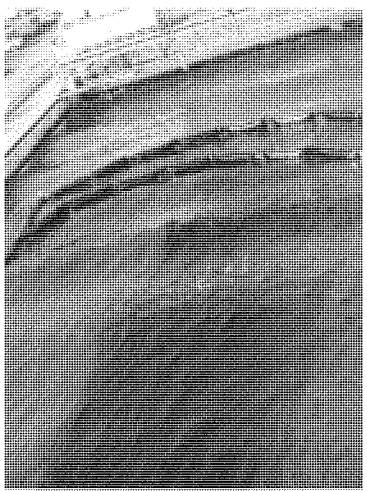
Visual Effectiveness = 1



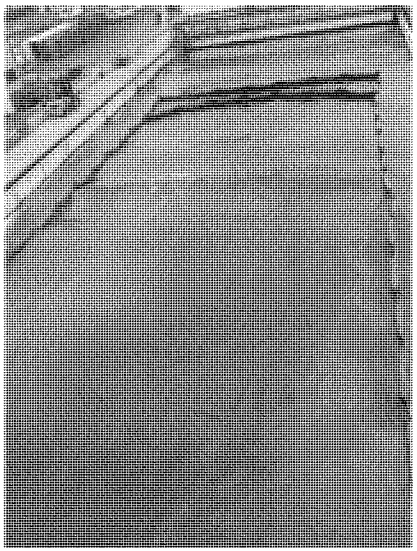



Visual Effectiveness = 3





Visual Effectiveness = 4



# SMART Tier 2 - Fluorometry

- Dissolved unsaturated and aromatic hydrocarbons, when excited by light waves at 280-320 nm, emit photons (fluoresce) at characteristic wavelengths. Aromatic hydrocarbons emit at about 340 nm; saturated hydrocarbons at about 445 nm. The size of the signal relates to the concentration of each fraction.
- Tier 2 SMART procedure makes use of this characteristic. Deploying a fluorometer by boat, the monitoring team samples at a depth of 1 to 2 m along transects through sections of the slick before and after dispersant spraying.

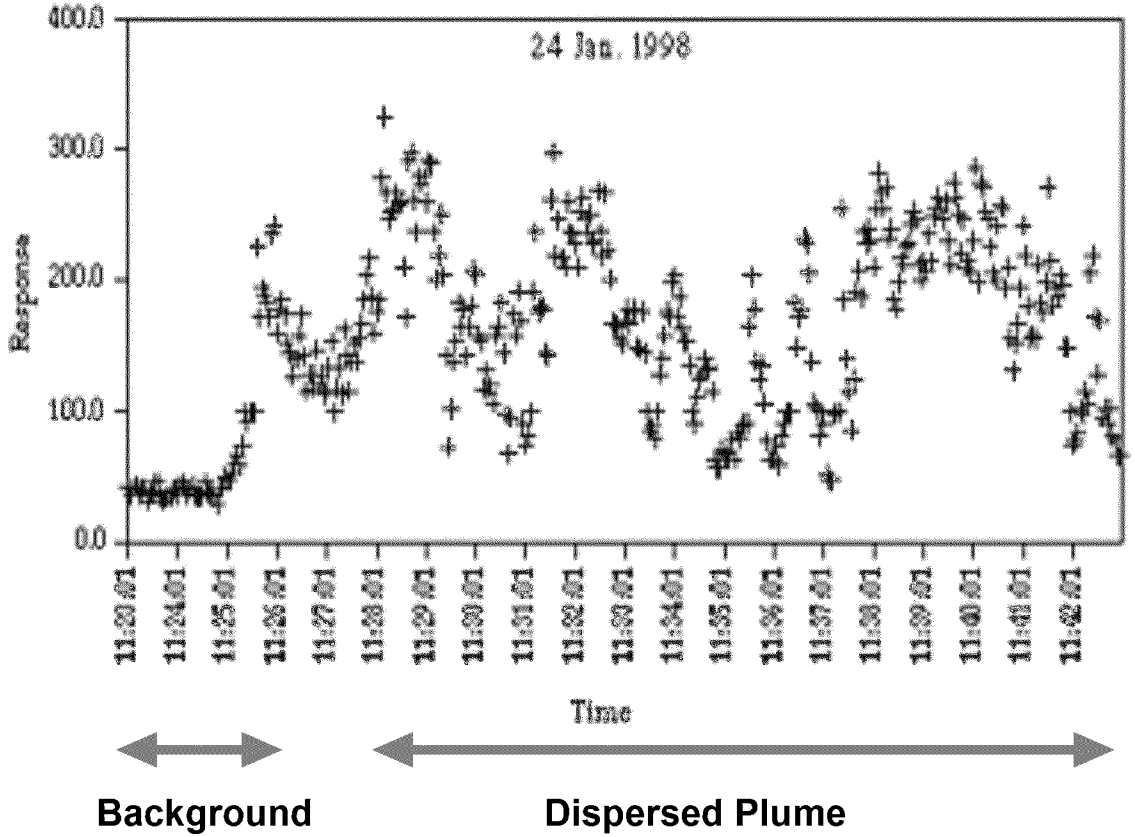
# SMART Tier 2 – Fluorometry (cont'd.)

- Vessel tows fluorometer outside the oil plume and bisects the oil plume to get a baseline of natural dispersability.
- Aircraft applies dispersant over target area.
- Dispersant applications are judged to be effective if fluorometer readings under treated slicks are at least 5 times greater than under untreated slicks (i.e., under the slick prior to treatment).
- Grab samples are taken from the water stream or by Kemmerer at predetermined intervals for post-event calibration of the fluorometer using the actual oil spilled and for Tier 3 analysis if required.

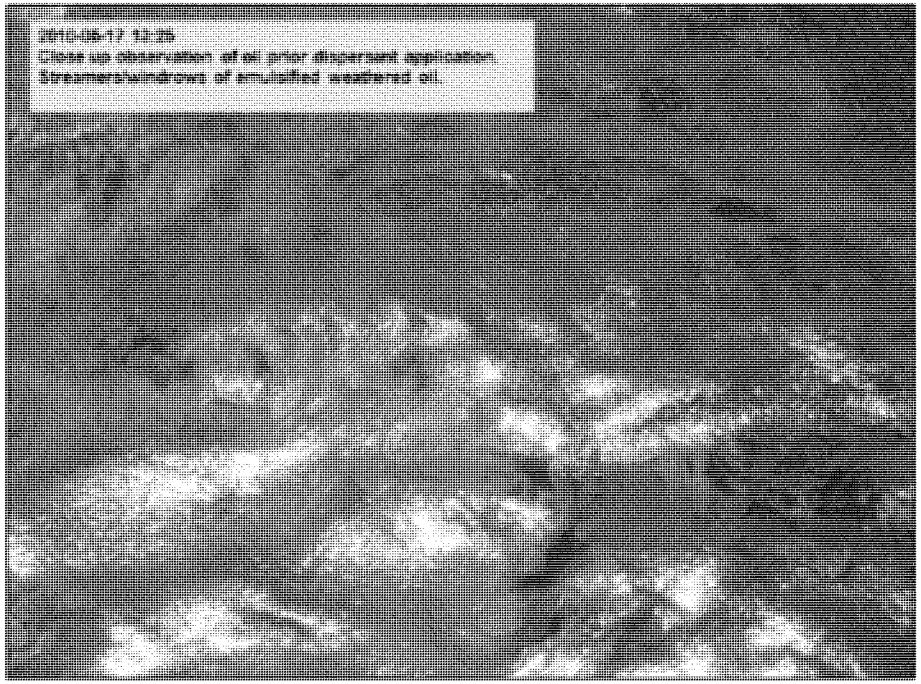
# Steps for SMART Tier 2 - Fluorometry

- Vessel tows fluorometer thirty minutes after dispersant application at a starting position outside the oil plume and bisects the plume to determine the effectiveness of the dispersant application.
- Vessel tows fluorometer sixty minutes after dispersant application at a starting position outside the oil plume and bisects the plume to determine the effectiveness of the dispersant application.

# Ideal Surface Application of Dispersant

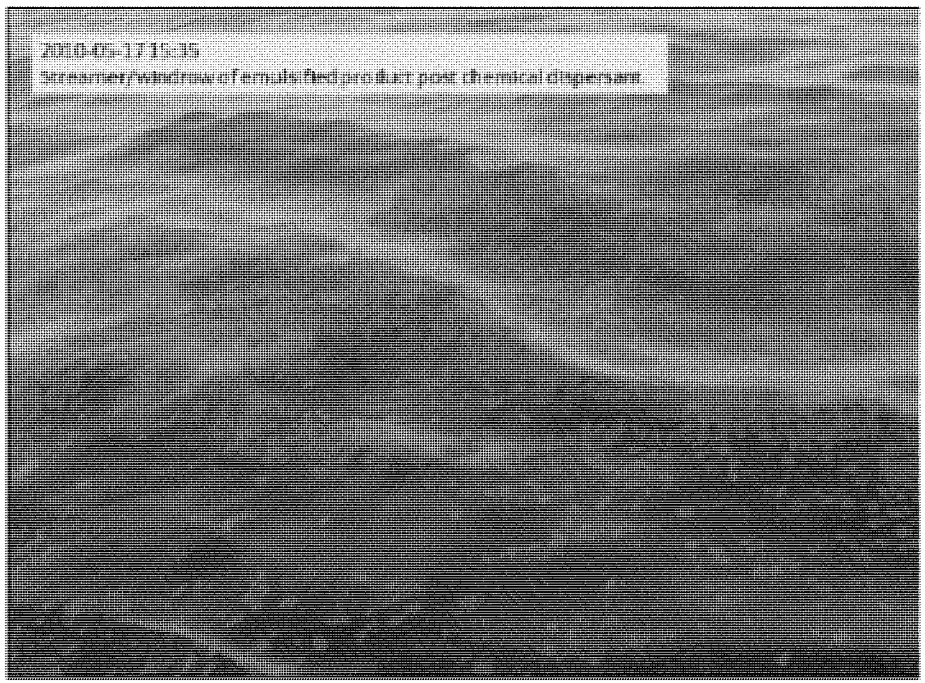



"Ideal" Fluorometry Trace from Historical Record




What does it look like?

**Data to date show dispersant effectiveness is consistent with our expectations**



# Choosing your Weapons for SMART Tier 2

- Fluorometers
- Particle Counters
- Bubble Size Indicators

Turner AU 10 Fluorometer
The “Old”

Turner Cyclops C6 Fluorometer
The “New”

# Turner C3 Fluorometer

"Weapon of Choice" in the Gulf

The Turner C3 fluorometer (excitation wavelength of 320 nm and emission wavelength of 400-600 nm) was towed by boat through the dispersed oil plume at 1-m and 2-m depths to make measurements of the dispersed oil plume both within the plume and up to 50-m outside the plume.

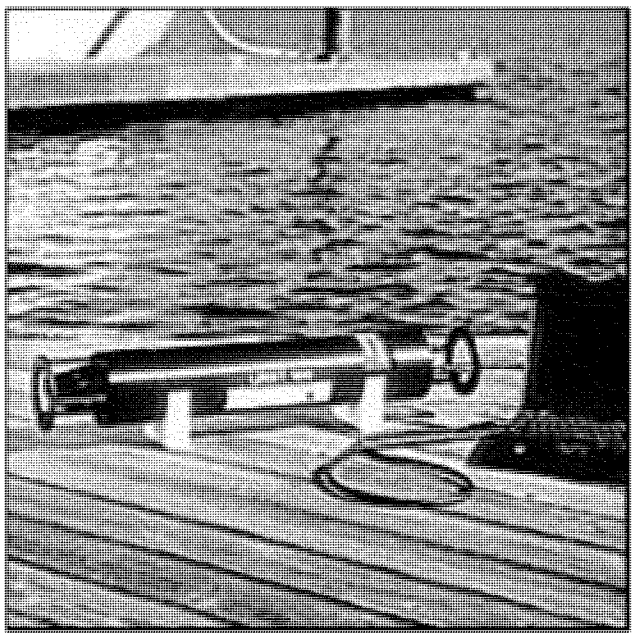
# BUBA Buster / Wetstar x GPS

- In-situ fluorescence detector combined with GPS
- Simple setup
- Continuous monitoring along transects
- Provides spatially-registered estimates of concentrations

TAMU FL3 and LISST-100X at Ohmsett

# Sequoia Particle and Particle-size Analyser

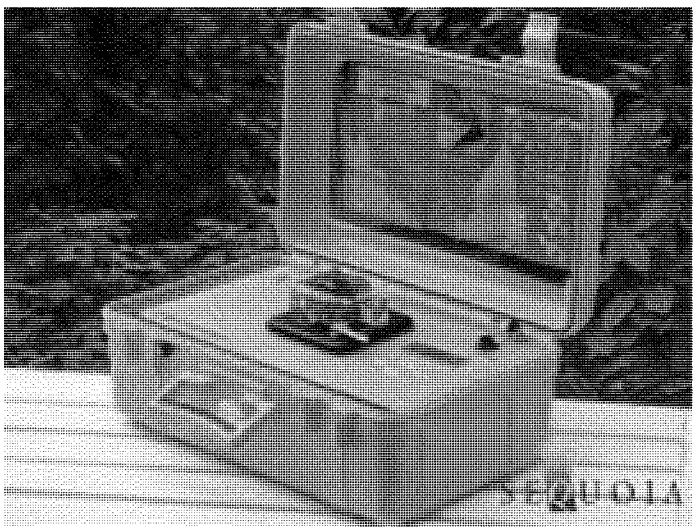
- Measures both oil droplet abundance and particle size in the range of 2.5 – 500 microns
- In-situ measurement
- Little set up needed
- Requires “blank”
- Needs clean water standard
- Continuous monitoring on transects
- Laser *In-Situ* Scattering and Transmissometry (LISST) instrument.



**LISST–100X Type-C**

# Sequoia On-Board Analysis

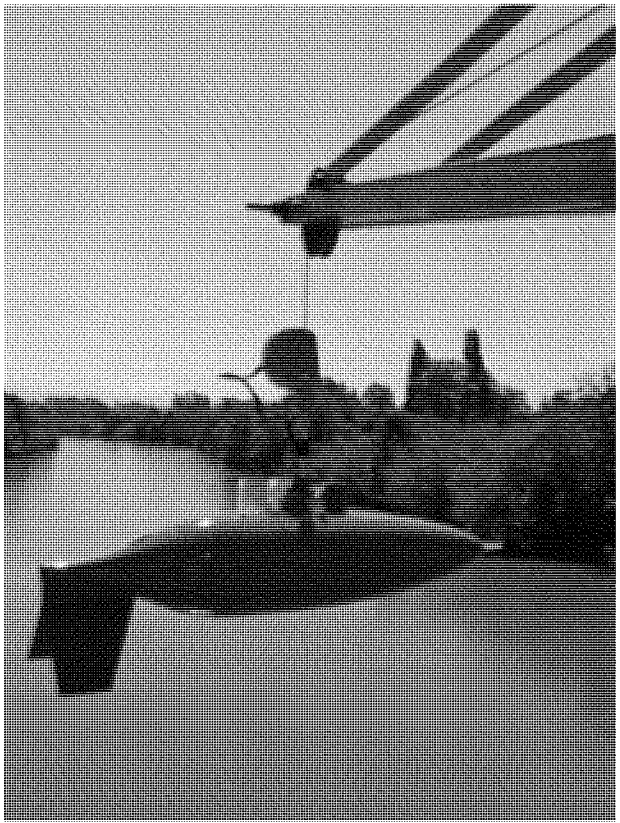
- Ex-situ particle-size analyser
- Analytical capability of LISST 100, but in ex-situ format
- Continuous monitoring
- Requires pump on effluent side
- Requires “blank”
- Amenable to post-calibration



**Sequoia Steam-Side**

# Sequoia Towable

- Towable in-situ particle-size analyser
- Analytical capability of LISST 100, but in easily towable
- Designed for freshwater,but could be set up form marine use

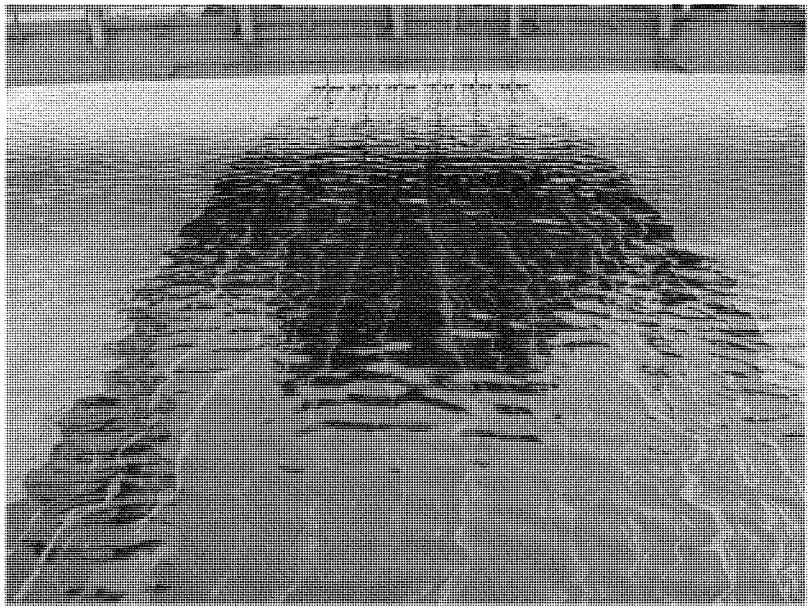


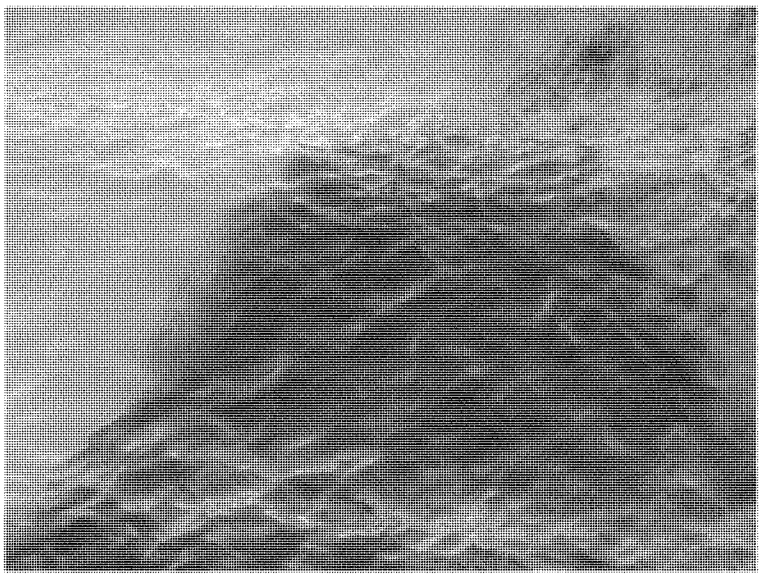
**Sequoia SL**

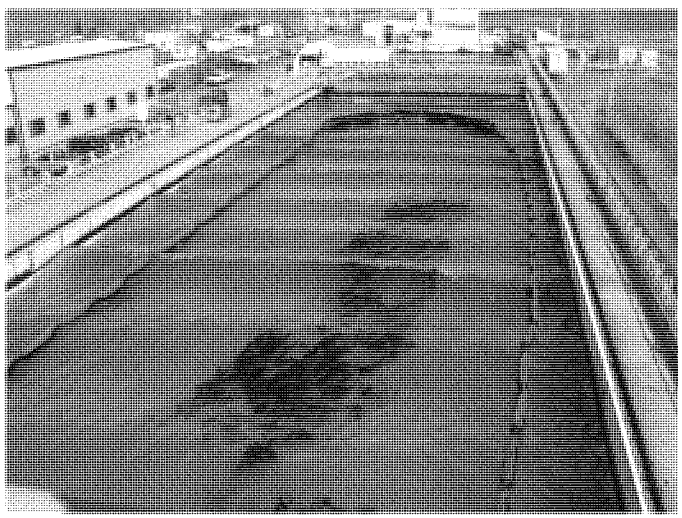
# Summary of New Items
## Based on a presentation by Ken Trudel

| Instrument | Pre-Deployment Engineering & Peripherals | On-Site Set-up and Calibration | Weight | Cost | Global Positioning System |
|---|---|---|---|---|---|
| Turner 10AU | Pump, power,hose, down-rigger | Assembly, calib w dye and/or oil | 35 lb Fluorometer only | $ 16 K | Extra |
| BUBA Buster | In-situ | Little set up; No user calib.; Diesel Standard | | $ 4K/ Unit Based on CDOM cost | Included |
| LISST -100X | In-situ | Blank | 25 lbs | $ 29.5 K/ Unit | Extra |
| LISST Stream-Side | Pump, power,hose, down-rigger | Blank | 15 lbs | $ 15K/ Unit | Extra |
| LISST SL | In-situ | Blank | 35 lbs | $ 35K/ Unit | Extra |
| Turner C3 | In-situ | Intuitive Calibration | 3.6 lbs | $ 8.5 K | Extra |

# Testing of Equipment at OHMSETT



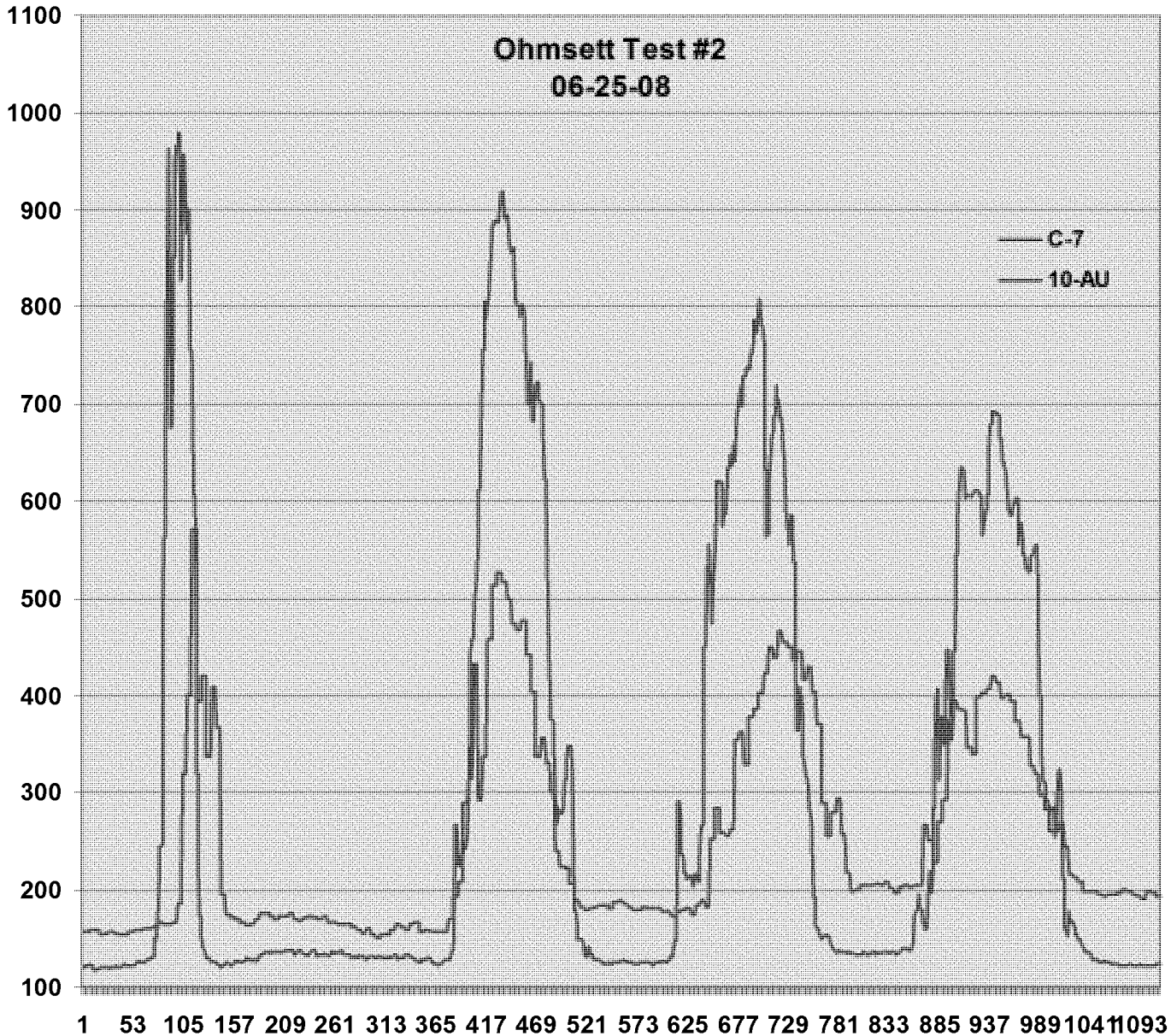




# Results of AU-10/Cyclops Comparison at OHMSETT June 2008

**Brian Parscal <brian@cleanislands.org>**

- Two tests were conducted on June 25th.
- The 10-AU was calibrated according SMART protocol standards while the C-7 was set to collect raw data on the medium gain setting. That most likely explains the difference in amplitude between the two.
- The C-7 (Cyclops) can detect dissolved oil in sea water and considering its ease of use, may be a good candidate for the SMART program.

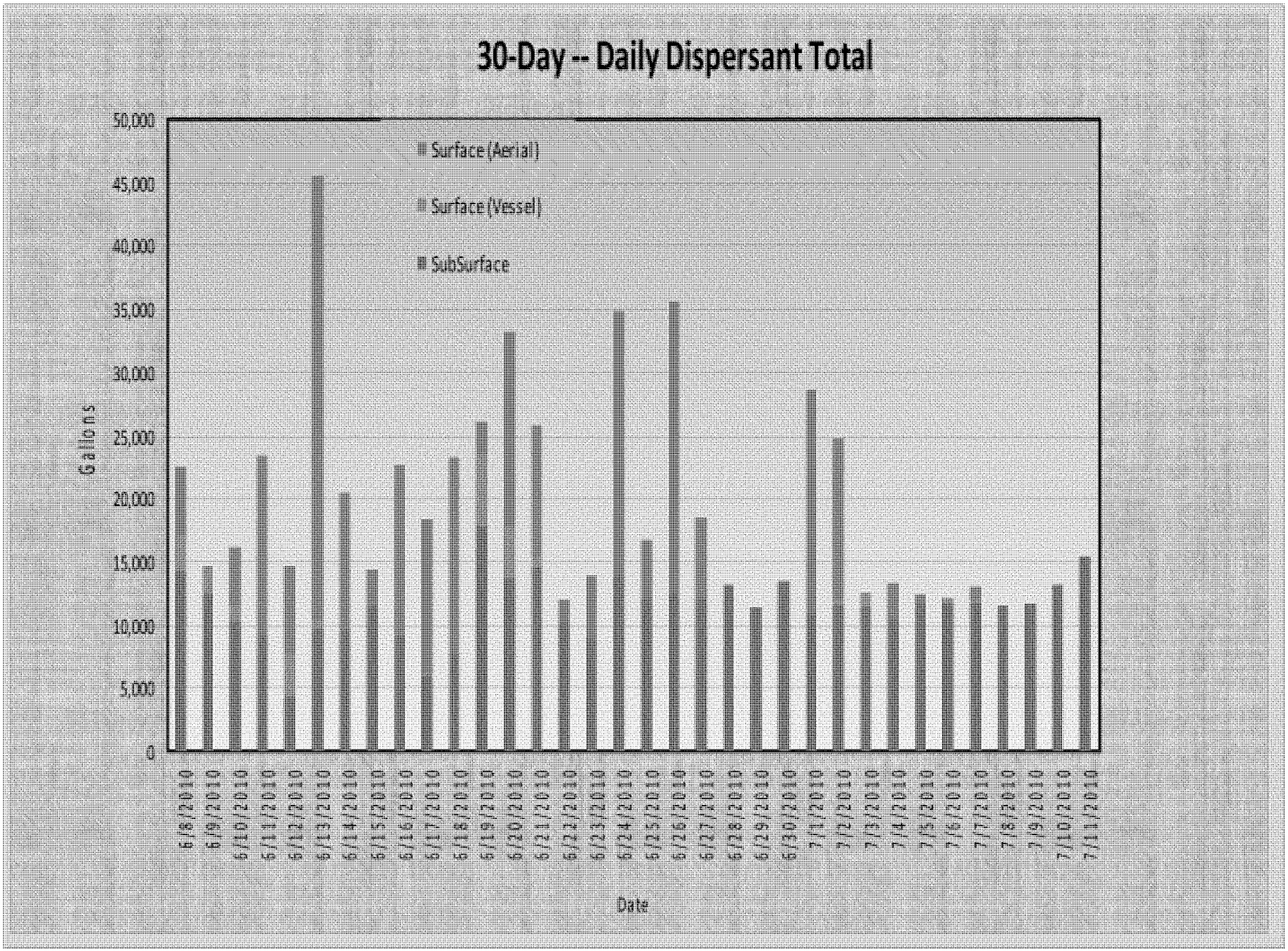

Ohmsett Test #2
06-25-08
C-7
10-AU
1100
1000
900
800
700
600
500
400
300
200
100
1 53 105 157 209 261 313 365 417 469 521 573 625 677 729 781 833 885 937 989 1041 1093

# Pros and Cons of Tier 2

- Fluorometry using a fixed wavelength is useful since it responds well to the dispersant concentration.
- Dispersed oil concentration and droplet size distribution is a very good indicator of dispersion effectiveness.
- Fluorometry cannot determine how the oil fingerprint is changing and what oil fractions actually are being dispersed; multiple emission wavelengths would be a better indicator of dispersed fractions.
- Small droplet size (<70 microns on nm) indicates good dispersion, and research indicates very fine (20 nm) particles are a strong indicator of chemical dispersion at moderate turbulence.
- Under the turbulent conditions of an expanding HC gas release at 152 atm, a stable emulsion might be generated mechanically.

# Surface Dispersant Application at the Deepwater Horizon

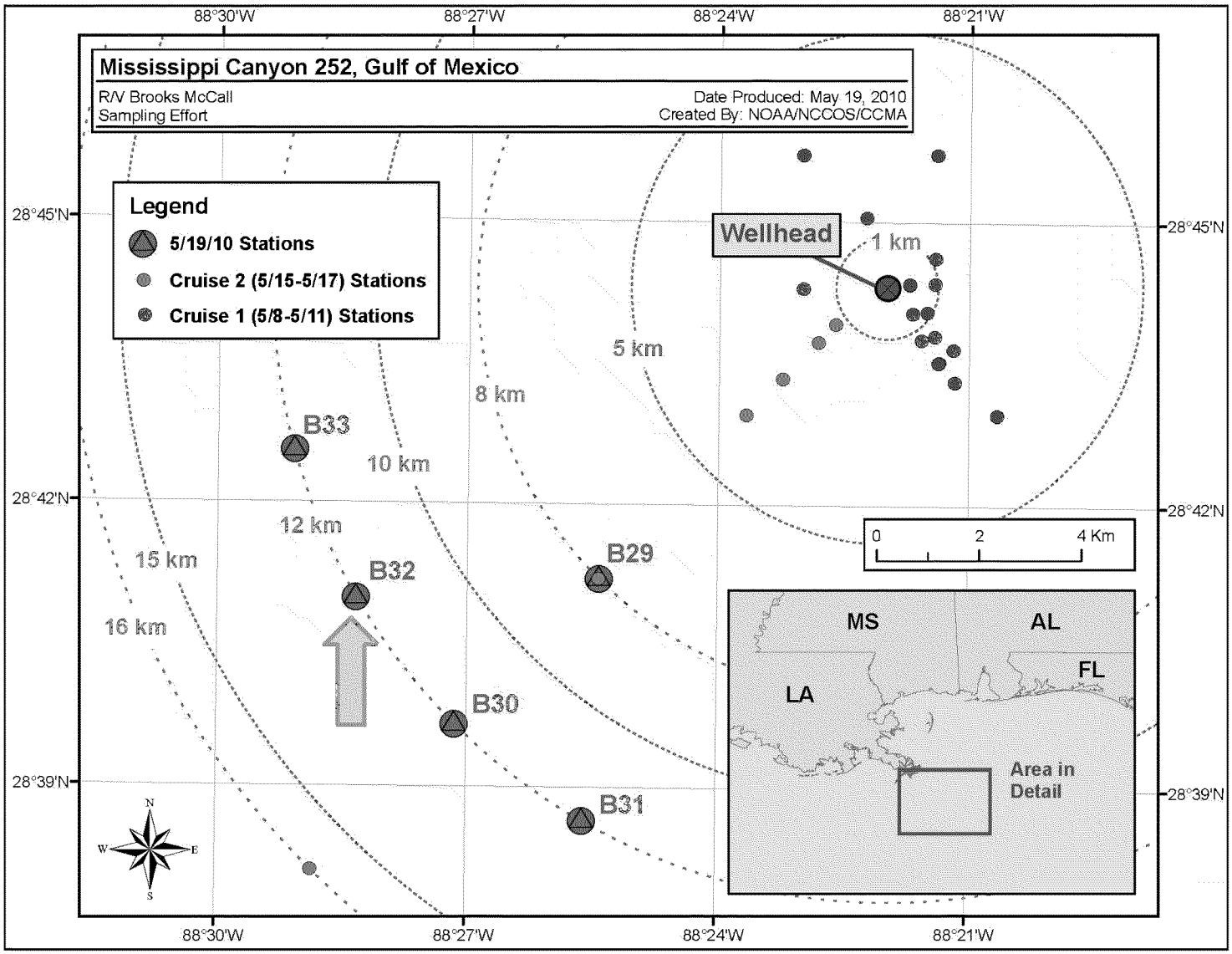
- Per RRT guidance application occurs >3 miles offshore and water depth of > 10 meters
- Applied primarily via aircraft
- As of 07/12/10
  - 404 sorties flown
  - 975,038 gallons sprayed
  - 305 sq miles covered (195,008 acres)


30-Day -- Daily Dispersant Total
Surface (Aerial)
Surface (Vessel)
SubSurface
Gallons
50,000
45,000
40,000
35,000
30,000
25,000
20,000
15,000
10,000
5,000
0
6/8/2010
6/9/2010
6/10/2010
6/11/2010
6/12/2010
6/13/2010
6/14/2010
6/15/2010
6/16/2010
6/17/2010
6/18/2010
6/19/2010
6/20/2010
6/21/2010
6/22/2010
6/23/2010
6/24/2010
6/25/2010
6/26/2010
6/27/2010
6/28/2010
6/29/2010
6/30/2010
7/1/2010
7/2/2010
7/3/2010
7/4/2010
7/5/2010
7/6/2010
7/7/2010
7/8/2010
7/9/2010
7/10/2010
7/11/2010
Date

# Field Application
# DWH Oil Spill
# Brooks-McCall Cruise
# May 19, 2011

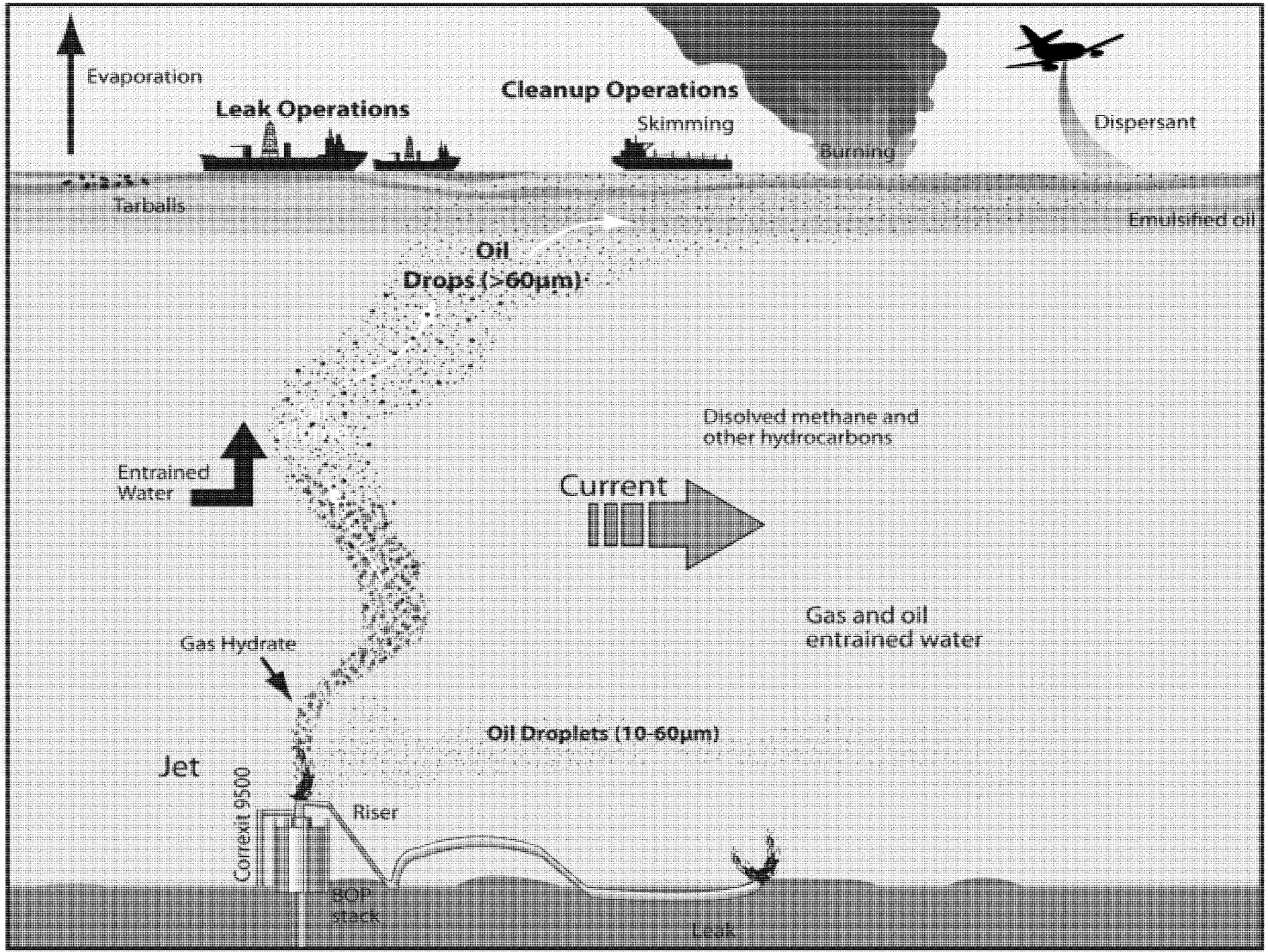
## Conductivity, Temperature, Density (CDT) Data plus Fluorometry Traces

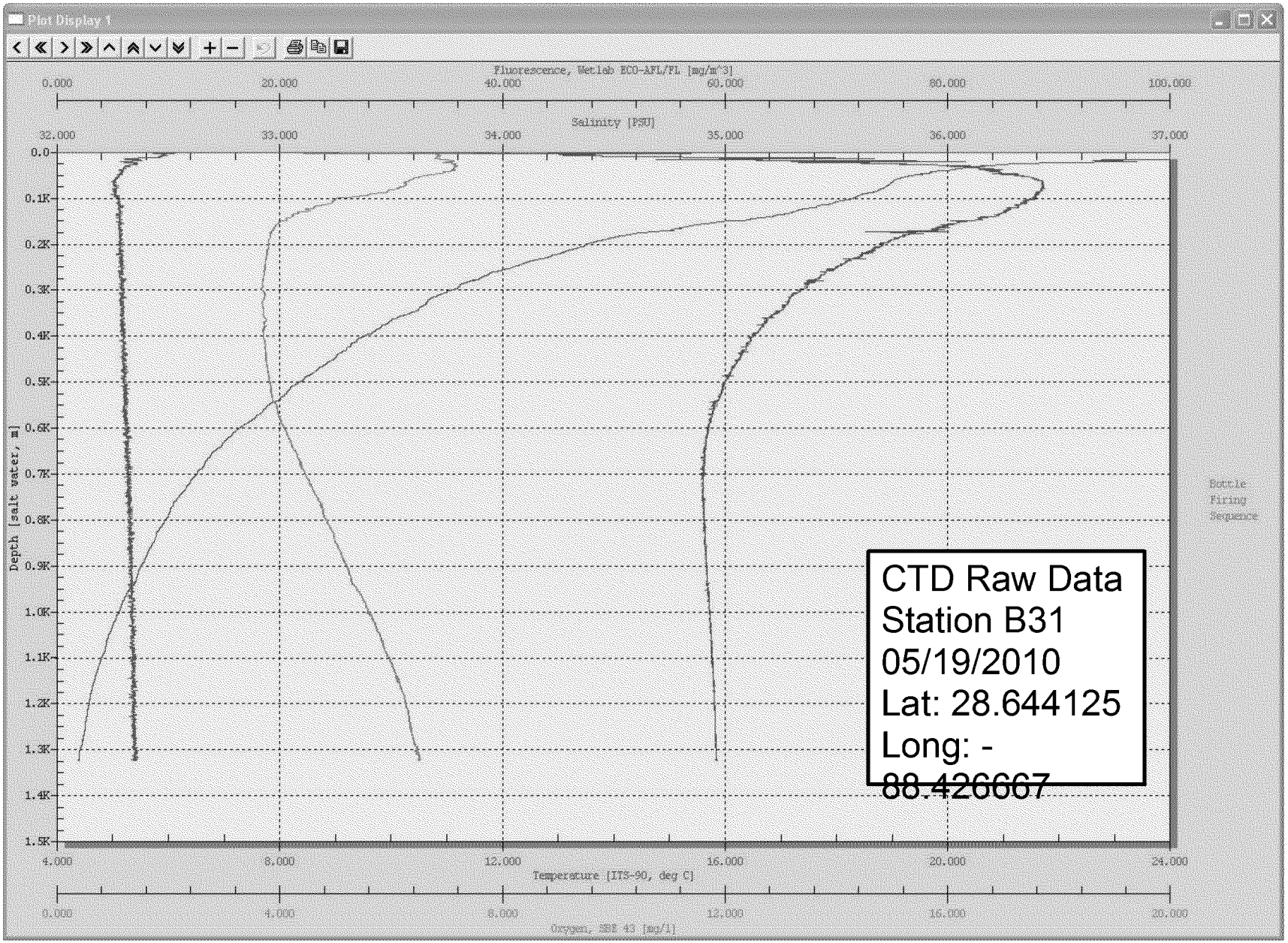
# Sampling Locations

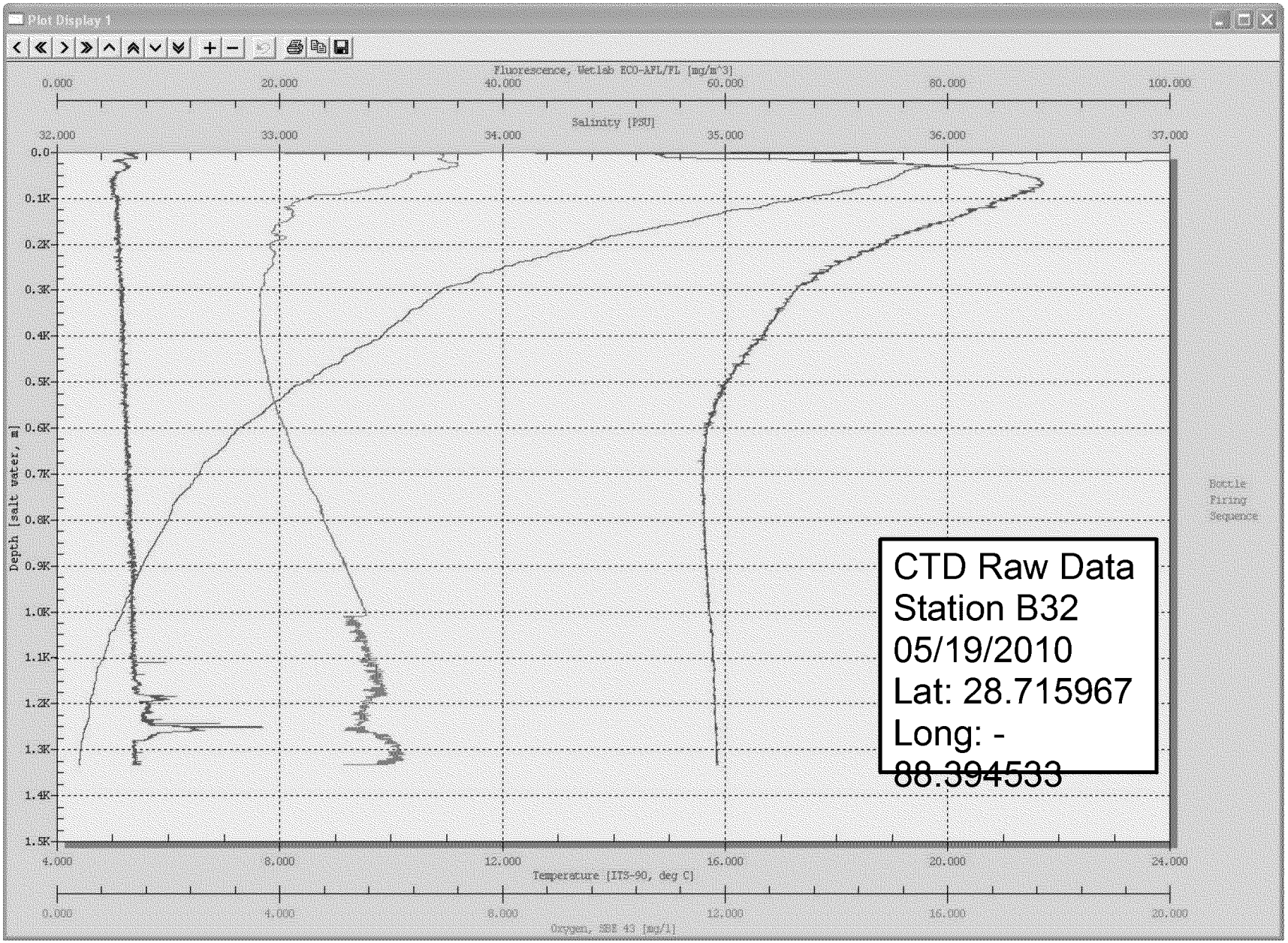


# On-Board Fluorometry

- Two fixed wavelength UV fluorometers were employed in tandem to determine Fluorescence Intensity Ratios (FIRs).
- One fluorometer was equipped with a pair of wavelength filters allowing excitation at 280 nm and emission at 340 nm.
- The second fluorometer was equipped with the same 280 nm excitation filter and a longer (445 nm) wavelength.
- FIRs were then calculated from fluorescence intensity at 340 nm divided by intensity at 445 nm.

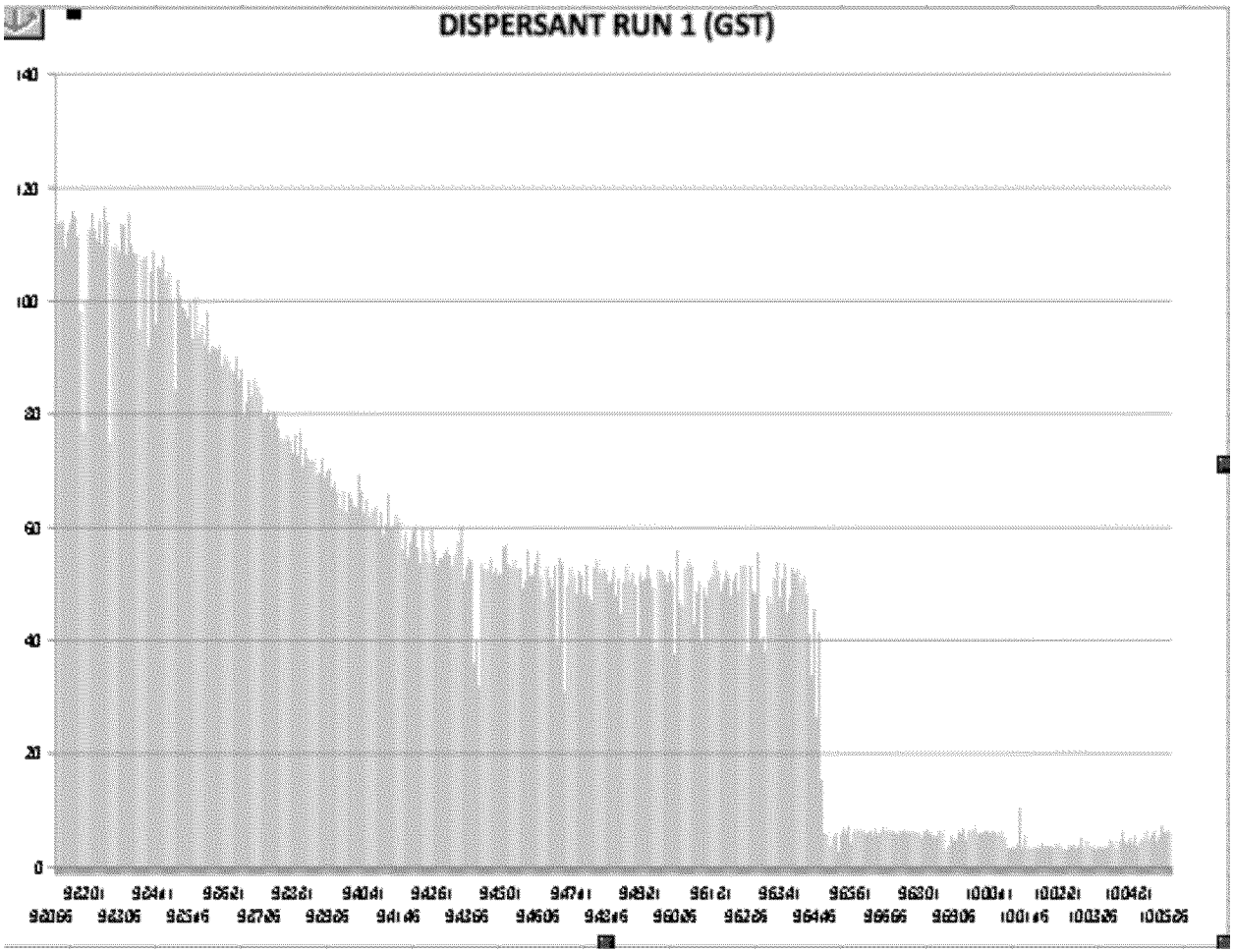

Evaporation
Leak Operations
Cleanup Operations
Skimming
Burning
Dispersant
Tarballs
Emulsified oil
Oil
Drops (>60µm)
Disolved methane and
other hydrocarbons
Entrained
Water
Current
Gas and oil
entrained water
Gas Hydrate
Oil Droplets (10-60µm)
Jet
Correxit 9500
Riser
BOP
stack
Leak


Plot Display 1
Fluorescence, Wetlab ECO-AFL/FL [mg/m^3]
0.000
20.000
40.000
60.000
80.000
100.000
Salinity [PSU]
32.000
33.000
34.000
35.000
36.000
37.000
Depth [salt water, m]
0.0
0.1K
0.2K
0.3K
0.4K
0.5K
0.6K
0.7K
0.8K
0.9K
1.0K
1.1K
1.2K
1.3K
1.4K
1.5K
Bottle Firing Sequence
CTD Raw Data
Station B31
05/19/2010
Lat: 28.644125
Long: -88.426667
4.000
8.000
12.000
16.000
20.000
24.000
Temperature [ITS-90, deg C]
0.000
4.000
8.000
12.000
16.000
20.000
Oxygen, SBE 43 [mg/l]

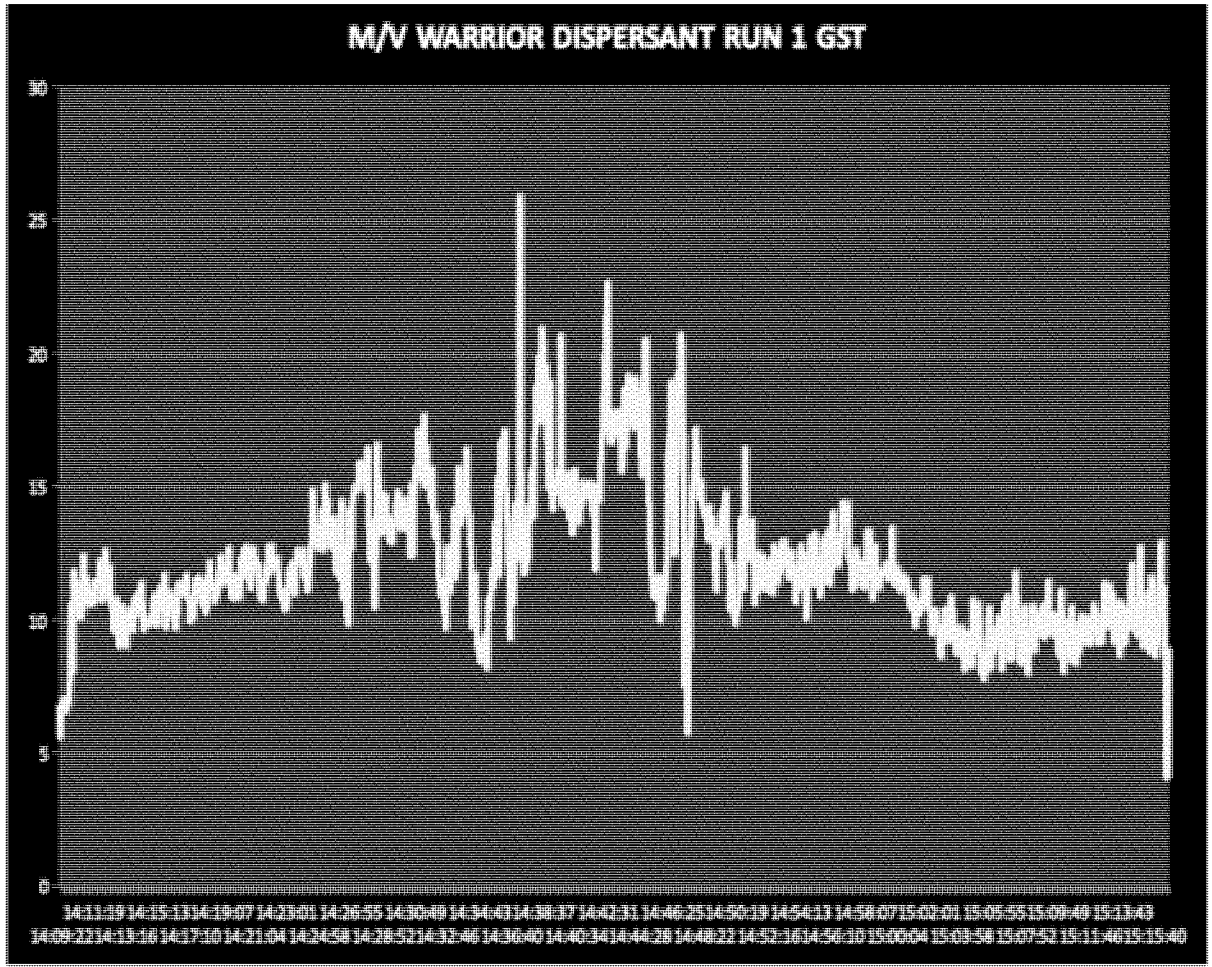

Plot Display 1
Fluorescence, Wetlab ECO-AFL/FL [mg/m^3]
0.000
20.000
40.000
60.000
80.000
100.000
Salinity [PSU]
32.000
33.000
34.000
35.000
36.000
37.000
Depth [salt water, m]
0.0
0.1K
0.2K
0.3K
0.4K
0.5K
0.6K
0.7K
0.8K
0.9K
1.0K
1.1K
1.2K
1.3K
1.4K
1.5K
Bottle Firing Sequence
CTD Raw Data
Station B32
05/19/2010
Lat: 28.715967
Long: -88.394533
4.000
8.000
12.000
16.000
20.000
24.000
Temperature [ITS-90, deg C]
0.000
4.000
8.000
12.000
16.000
20.000
Oxygen, SBE 43 [mg/l]

# SMART Tier 2
# Monitoring of Surface Application of Dispersant

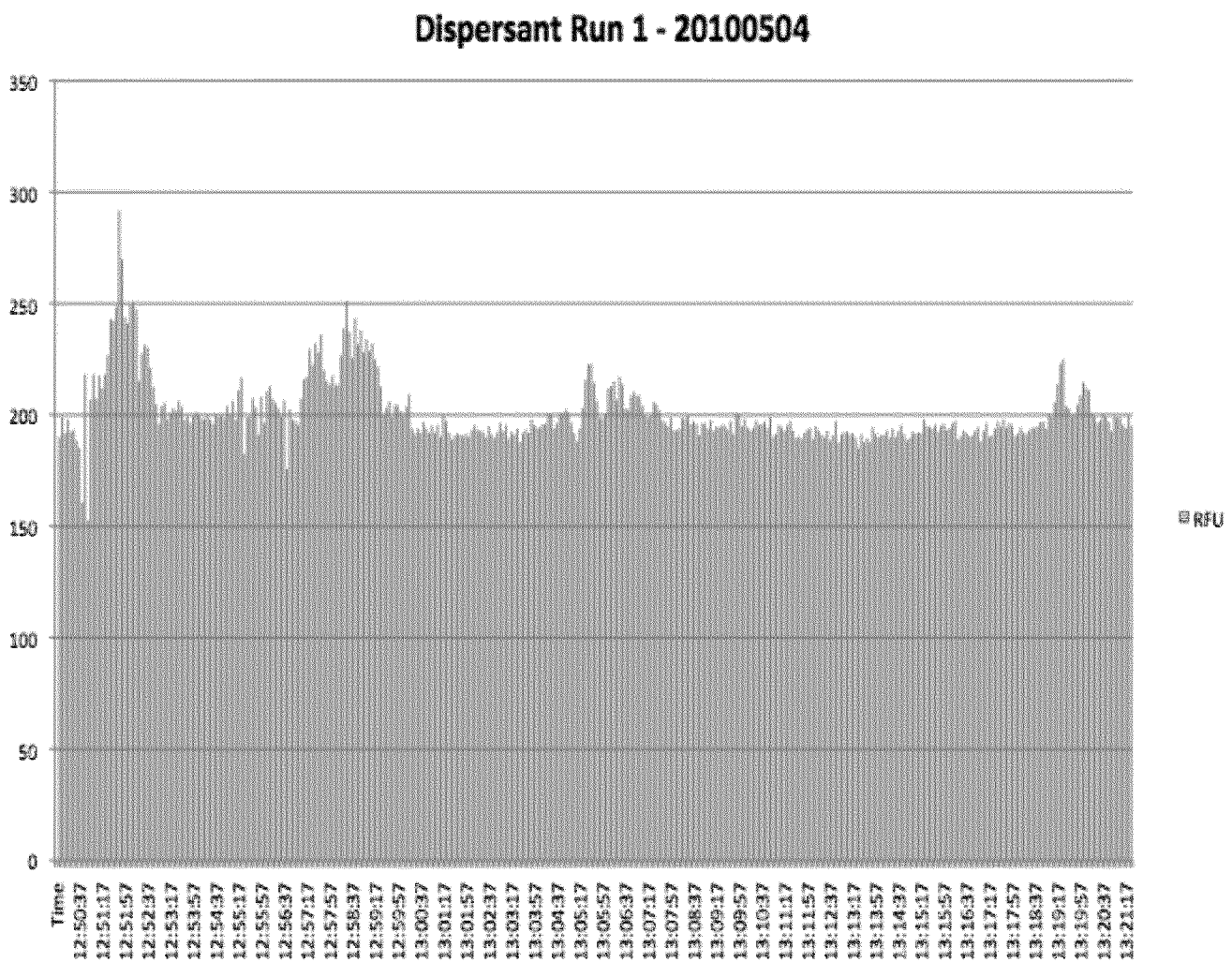
- A set of results was submitted to the HQ Science Group for assessment.
- The following 5 figures were used by EPA to determine that surface application of dispersant was not effective.
- The 6th figure is a good example of a fluorometry trace which compares mechanical and chemical dispersion near the surface.



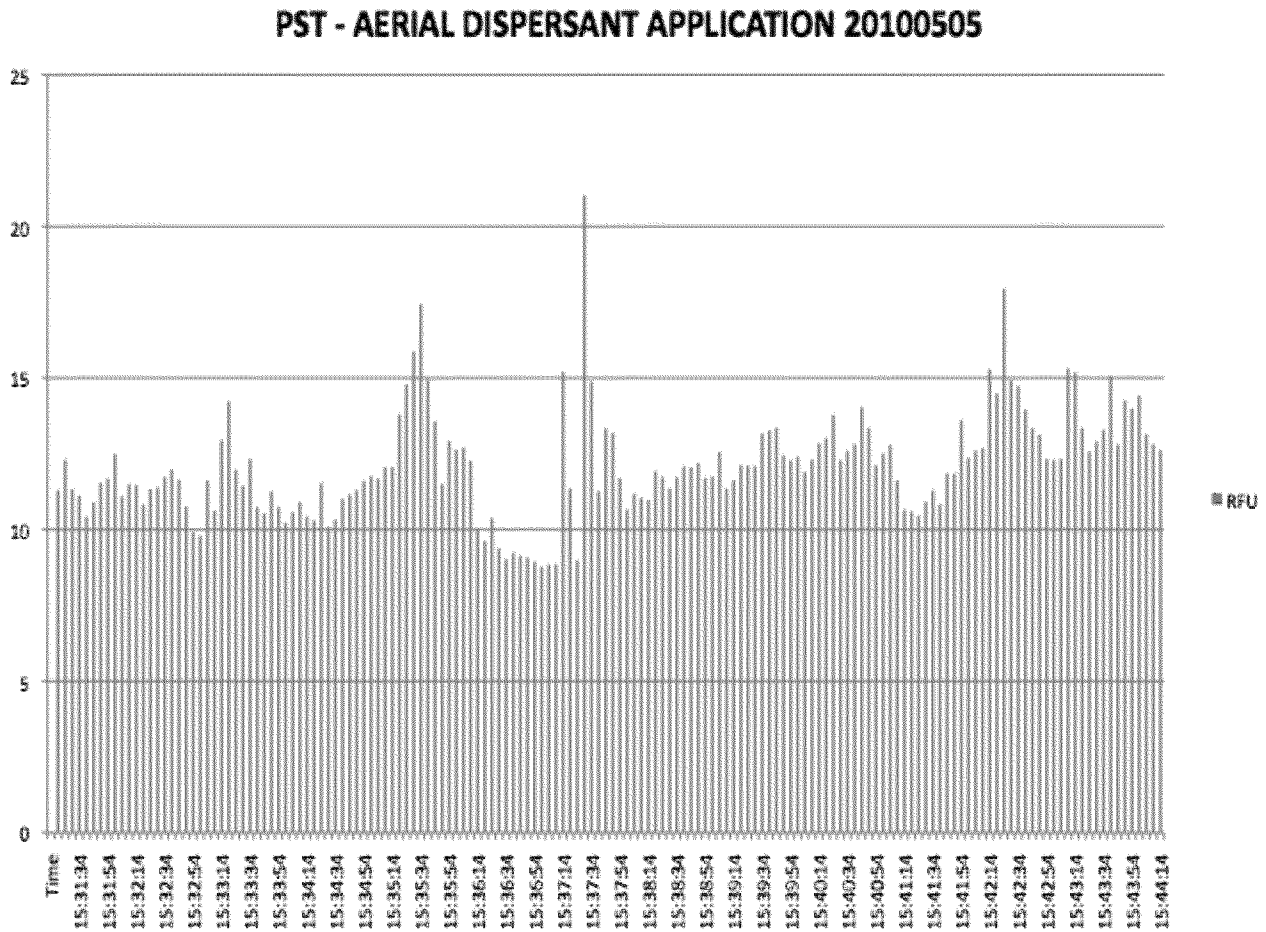

Increase of Fluorometry Reading >10x
(Almost 30x at Mid-plume)
Successful Application 4/28/2010




Unsuccessful Dispersant Application 4/28/2010

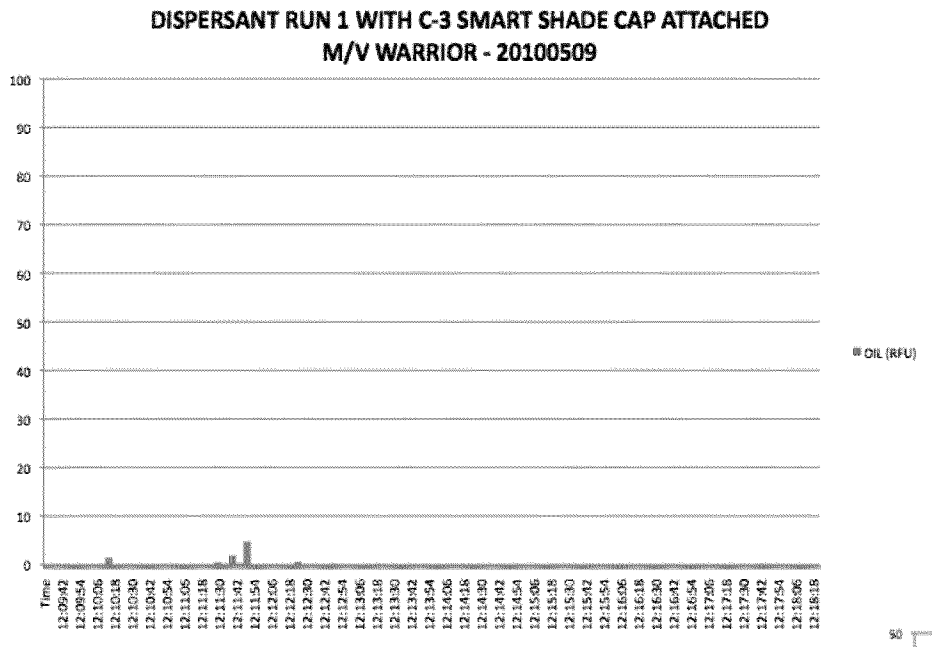


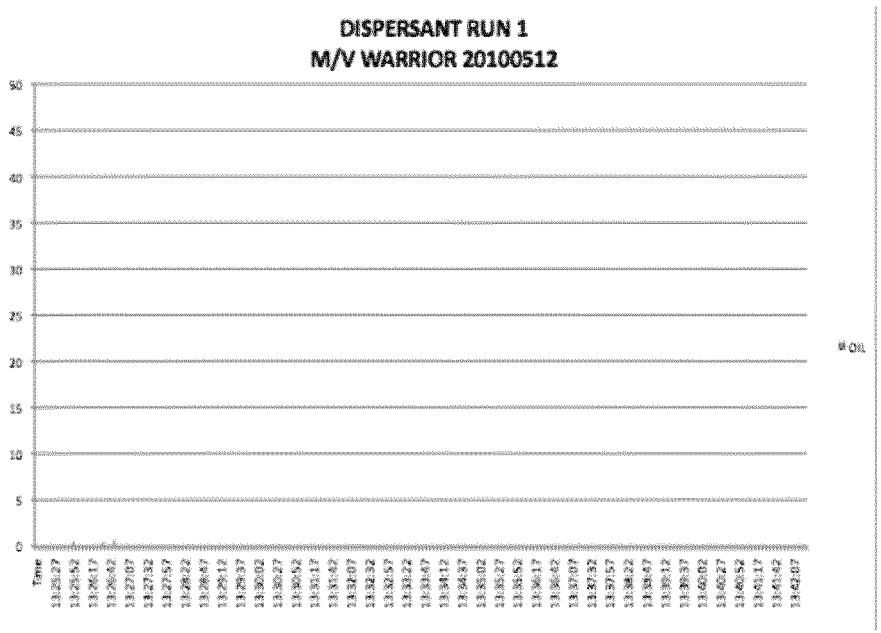

Unsuccessful Dispersant Application 5/4/2010

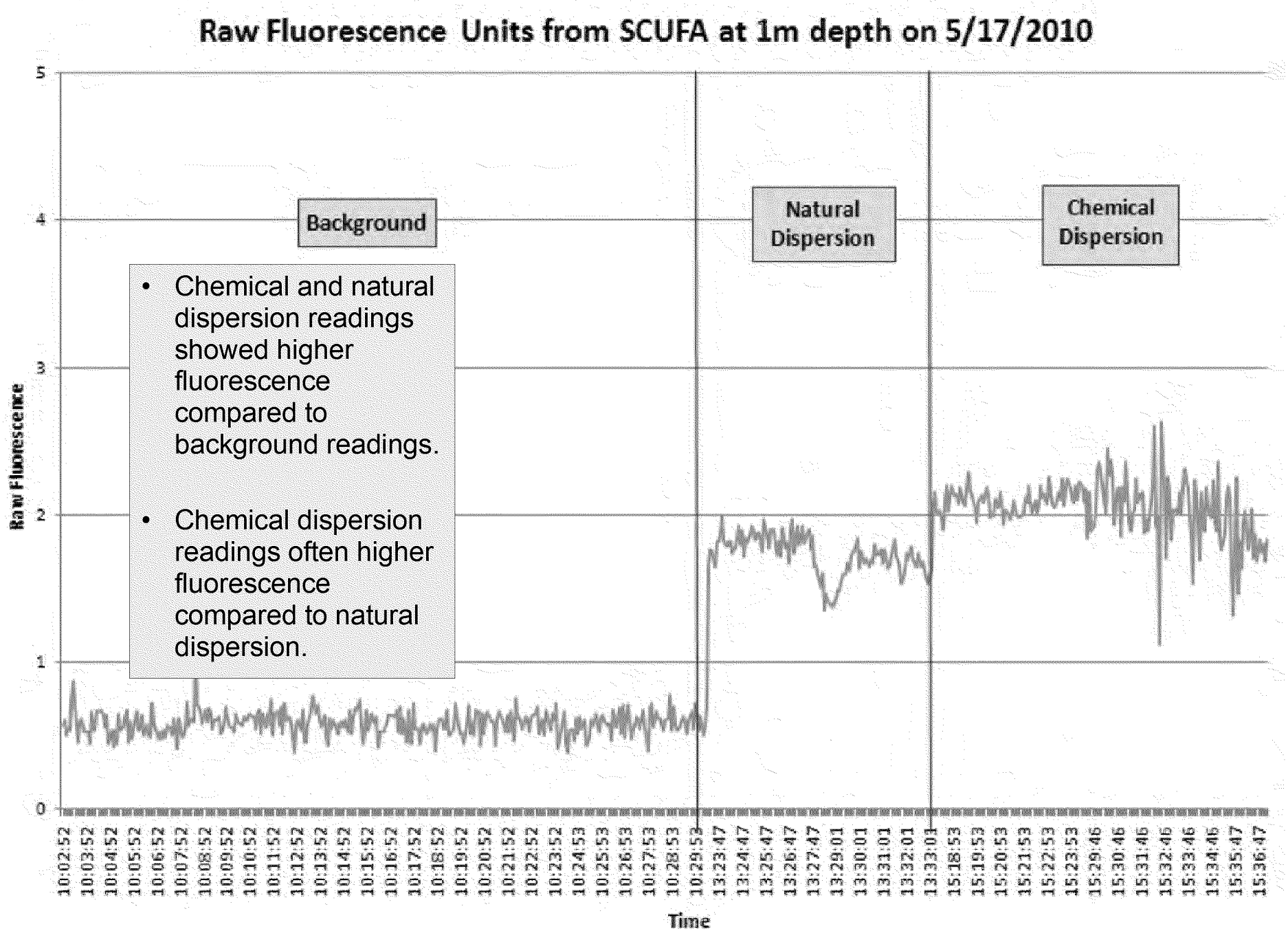



Unsuccessful Dispersant Application 5/5/2010

# Incomplete Fluorometry Data Runs of 5/9-10/2010




Raw Fluorescence Units from SCUFA at 1m depth on 5/17/2010
Background
Natural Dispersion
Chemical Dispersion
• Chemical and natural dispersion readings showed higher fluorescence compared to background readings.
• Chemical dispersion readings often higher fluorescence compared to natural dispersion.
Raw Fluorescence
Time

# So now we can judge for ourselves as to the "effectiveness" of dispersant application.

- How effective was the dispersant in removing the oil from the environment?
- How effective was the dispersant in reducing the environmental impact?
- In other words, where is the rest of the oil and dispersant and what kind of toxic residuals can we expect?

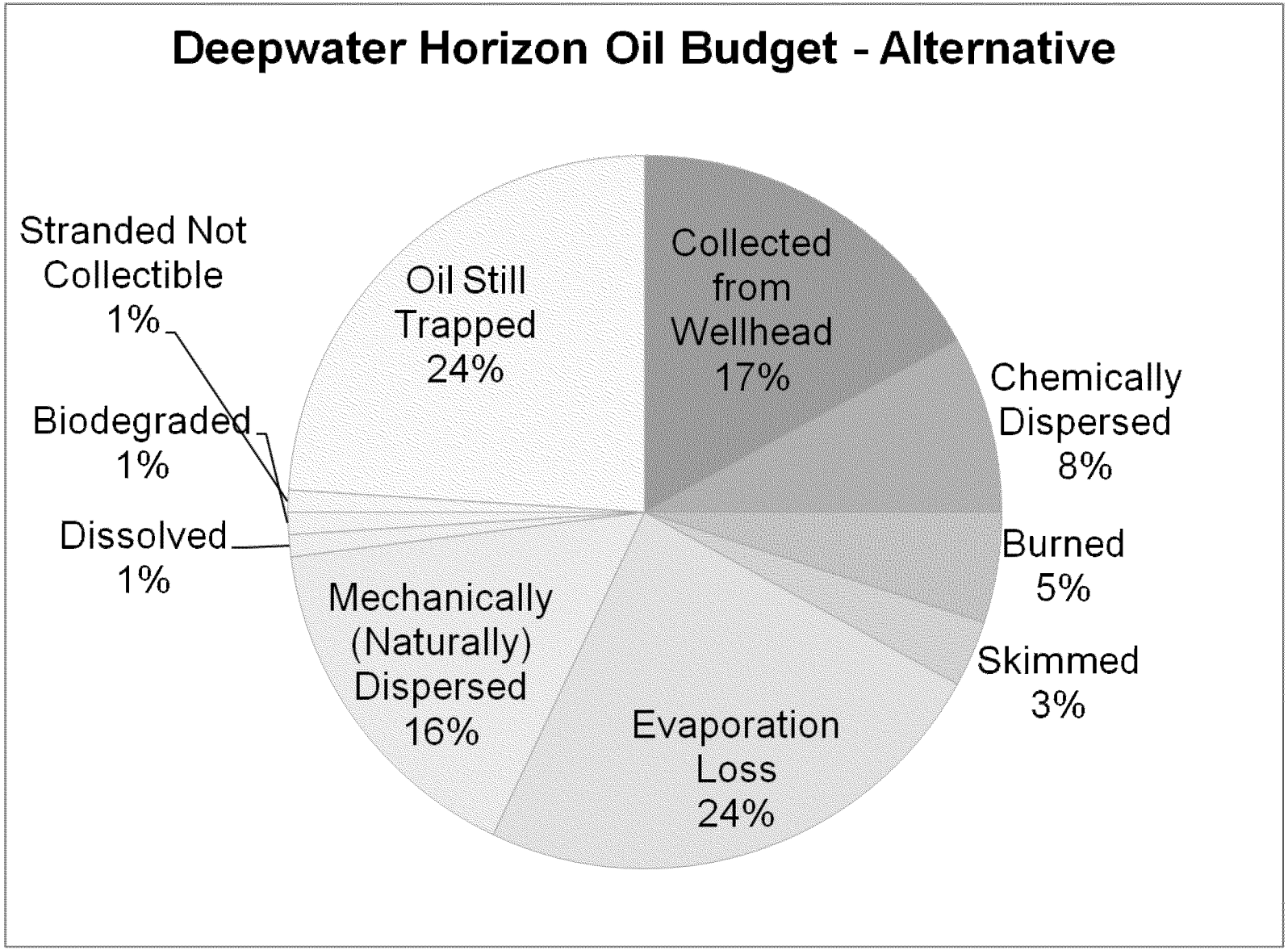
# Deepwater Horizon Oil Budget Quantities

ERT Edition of NOAA/USGS Budget

| | Fraction | MG |
|---|---|---|
| Collected from Wellhead | 0.17 | 35.0 |
| Chemically Dispersed | **0.08** | **16.5** |
| Burned | 0.05 | 10.3 |
| Skimmed | 0.03 | 6.2 |
| Evaporation Loss | 0.24 | 49.4 |
| Mechanically (Naturally) Dispersed | **0.16** | **32.9** |
| Dissolved | 0.01 | **2.1** |
| Biodegraded | 0.01 | 2.1 |
| Stranded Not Collectible | **0.01** | **2.1** |
| Oil Still Trapped | **0.24** | **49.4** |
| Residual Still in the Gulf System | 0.50 | **100.8** |

Actually, a 25% recovery is remarkable, and if we count the 8% chemically dispersed, 33% mitigation is quite a feat!!

# Modified Oil Budget



# So why go to SMART Tier 3 and sample?

- The EPA and the Natural Resource Trustees need to be concerned with the oil spill impacts which are not caused by the “coating effect” of the oil itself.
- During the turbulence of many spills, including mixing from wind and wave action, oil can be dispersed mechanically, and soluble components of oil can partition into the water column.
- The EPA and the Natural Resource Trustees need to be concerned with the oil spill impacts which are not caused by the “coating effect” of the oil itself.
- This involves chemical analysis, which triggers the need for SMART Tier 3.

- The Canadians and EPA's ORD have taught us that the lighter and more soluble oil components are more easily dispersed chemically. These are also the more toxic and biodegradable components, thus these are the most likely to cause environmental impact. In a localized or confined area, concentrations could build up and either toxicity, oxygen deficiency, or both could exert undesirable effects.
- Biodegradation potential of the suspended and dispersed residual oil and dispersant is also related to the chemical components, rather than on the broad categories of petroleum hydrocarbons or fluorescible organics.

- The NOAA SQuIRTs anticipate these problems and provide parameters and analytical method citations to address them. Many of the chemicals listed do not relate to oil spills, but some refer to the volatile and semivolatile components of crude and refined products.

- Since different oils have different relative concentrations of these fractions, assessing the environmental risk from the dispersible fraction requires that we either know what is in the originally-spilled oil or measure the byproducts in solution or suspension. The Environment Canada Catalog of Oil Properties can help predict this fraction.

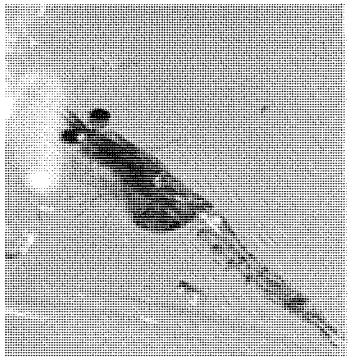
- National Academy of Sciences' 1972 Blue Book is still useful for water quality criteria relative to oil spills.

# SQuiRTs are for NOAA Hazmat screening-level use, but…

- Screening levels are based on EPA's Water Quality Criteria for acute exposure (highest 1 hour average, not to exceed once every 3 years). (This is effectively a grab sample.)
- For Semivolatile PAH, the concentration ranges between 7.7 and 3,980 ppb (ug/L)
- For Volatile Aromatics (BTEX) ranges between 530 to32,000 ppb.
- For Total Petroleum Hydrocarbons, there is no SQuiRT listed, but EPA's Method 8015B (GC/FID) is specified.
- SQuiRTs, are available on NOAA's website:

http://response.restoration.noaa.gov

## Results of 48 hour acute toxicity tests of 8 dispersants to the Gulf of Mexico invertebrate, mysid shrimp (*Americamysis bahia*)

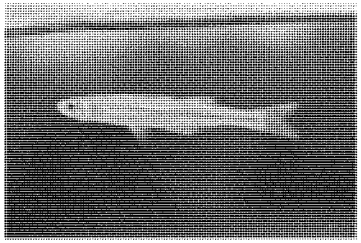


| Dispersant | This Study LC50 (ppm) [95% CI] | Toxicity Category | NCP Product Schedule LC50 (ppm) [95% CI] |
|---|---|---|---|
| Dispersit SPC 1000 | 12 [10-14] | Slightly Toxic | 16.6 [14.1-19.6] |
| Nokomis 3-AA | 30 [27-34] | Slightly Toxic | 20.2 [17.4-22.8] |
| **Corexit 9500A** | **42 [38-47]** | **Slightly Toxic** | **32.2 [26.5-39.2]** |
| Nokomis 3-F4 | 42 [38-47] | Slightly Toxic | 32.2 [28.4-36.5] |
| ZI -400 | 55 [50-61] | Slightly Toxic | 21.0 [17.9-24.5] |
| Sea Brat #4 | 65 [57-74] | Slightly Toxic | 14.0 [±10.4] |
| Saf-Ron Gold | 118 [104-133] | Practically Non-Toxic | 63.0* [52.9-75.1] |
| JD-2000 | 788 [627-946] | Practically Non-Toxic | 90.5* [76.1-108] |

* Classified as slightly toxic according to values provided in NCP Product Schedule

http://www.epa.gov/bpspill/dispersants-testing.html

## Results of 96 hour acute toxicity tests of 8 dispersants to the Gulf of Mexico fish, inland silverside (*Menidia beryllina)*



| Dispersant | This Study LC50 (ppm) [95% CI] | Toxicity Category | NCP Product Schedule LC50 (ppm) [95% CI] |
|---|---|---|---|
| Dispersit SPC 1000 | 2.9 [2.5-3.2] | Moderately Toxic | 3.5 [3.1-4.0] |
| Nokomis 3-F4 | 19 [16-21] | Slightly Toxic | 29.8 [24.0-35.4] |
| Nokomis 3-AA | 19 [17-21] | Slightly Toxic | 34.2 [29.2-37.95] |
| ZI -400 | 21 [18-23] | Slightly Toxic | 31.8 [28.7-35.1] |
| Saf-Ron Gold | 44 [41-47] | Slightly Toxic | 29.4 [25.2-34.3] |
| Sea Brat #4 | 55 [49-62] | Slightly Toxic | 30.0 [±16.2] |
| **Corexit 9500A** | **130 [122-138]** | **Practically Non-Toxic** | **25.2* [13.6-46.6]** |
| JD-2000 | >5,600 | Practically Non-Toxic | 407 [330-501] |

* Classified as slightly toxic according to values provided in NCP Product Schedule

http://www.epa.gov/bpspill/dispersants-testing.html

# SMARTer

- It is important to remember that in the rapidly changing conditions of spill response, flexibility and adaptability are essential for success. The sampling plan is dictated by many factors, including the availability of equipment and personnel, on-scene conditions, and the window of opportunity for dispersant application.
- The need for flexibility in sampling design, effort, and rapid deployment may dictate the nature and extent of the monitoring.
- To assist the monitoring efforts, it is important that the Unified Command agrees on the goals and objectives of monitoring and chooses the appropriate level of effort for the response.

# SMART Sampling and Analysis for Dispersant Application – A Final Message from the Old Timers

- Ken Biglane, the architect of the NCP and ERT, once said “I trust the oil I can see more than the oil I can't see.”
- Dr. Joseph P. Lafornara, 12/10/2003, quoted Ken and remarked on the Need for a National Dispersant Use Policy.
- The BP Deepwater Horizon Response showed that this policy is still needed.
- SMART performance data will be needed to craft a rational policy.

# Contact Information

- Allen.Harry@epa.gov
- www.epaosc.org/SMARTOSC/
- 732-321-6740 (ERT Main Number)
- 732-321-6660 (ERT Hotline)

**To:** Wilson, Gregory[Wilson.Gregory@epa.gov]; Matthiessen, Craig[Matthiessen.Craig@epa.gov]; Barron, Mace[Barron.Mace@epa.gov]; Principe, Vanessa[Principe.Vanessa@epa.gov]
**From:** Conmy, Robyn
**Sent:** Mon 4/13/2015 6:20:16 PM
**Subject:** RE: FYI - : BP dispersant toxic
DeLeo et al 2015_coral_dispersant_DSR II_just accepted version.pdf

Here's the paper. Keep in mind that it was just accepted online and there is a disclaimer that edits still may occur prior to the print release.

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

conmy.robyn@epa.gov

**From:** Wilson, Gregory
**Sent:** Monday, April 13, 2015 1:55 PM
**To:** Conmy, Robyn; Matthiessen, Craig; Barron, Mace; Principe, Vanessa
**Subject:** RE: FYI - : BP dispersant toxic

Just for everyone's reference, this is the EPA website I use to request articles:
http://intranet.epa.gov/hqchem/forms/article.html

Usually takes a couple of days....

**From:** Conmy, Robyn

**Sent:** Monday, April 13, 2015 1:51 PM
**To:** Matthiessen, Craig; Barron, Mace; Wilson, Gregory; Principe, Vanessa
**Subject:** RE: FYI - : BP dispersant toxic

If you hold off for an hour, I am getting the paper from some academic connections....

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

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**From:** Matthiessen, Craig
**Sent:** Monday, April 13, 2015 1:46 PM
**To:** Barron, Mace; Wilson, Gregory; Principe, Vanessa; Conmy, Robyn
**Subject:** RE: FYI - : BP dispersant toxic

Hi, Mace;

Here is a link to the Oceans article: http://www.eenews.net/stories/1060016566

And a link to the study paper:
http://www.sciencedirect.com/science/article/pii/S0967064515000740

Looks like you'd have to purchase it. However, the EPA library system may be able to get it.

And I forgot Michael retired. Thanks - Craig

**From:** Barron, Mace
**Sent:** Monday, April 13, 2015 1:38 PM
**To:** Matthiessen, Craig; Wilson, Gregory; Principe, Vanessa; Conmy, Robyn
**Subject:** Re: FYI - : BP dispersant toxic

Hi Craig: I read the summary below and the abstract, but don't have access to the paper.

Should I request through interlibrary loan from our librarian, or do you have a copy?

PS: Michael is retired, so I took him off this email.

Mace

---

**From:** Matthiessen, Craig
**Sent:** Monday, April 13, 2015 12:31 PM
**To:** Wilson, Gregory; Principe, Vanessa; Conmy, Robyn; Barron, Mace; Hemmer, Michael
**Subject:** FW: FYI - : BP dispersant toxic

Any thoughts? Thanks - Craig

**From:** Nichols, Nick
**Sent:** Monday, April 13, 2015 10:16 AM
**To:** Matthiessen, Craig; Oliveira, Beatriz; DeHaven, Leigh; Gioffre, Patricia; Howard, MarkW; Swackhammer, J-Troy
**Subject:** FYI - : BP dispersant toxic

FYI

**OCEANS:**

## Gulf spill cleanup dispersant more toxic to coral than oil -- study

Katherine Ling, E&E reporter

Published: Friday, April 10, 2015

The chemical dispersant used to break down the oil spilled in the 2010 Deepwater Horizon accident in the Gulf of Mexico is more toxic to coral than the oil, according to a study released on the eve of the fifth anniversary of the disaster.

The accident marked the first time that a dispersant was used below the ocean surface during an oil spill in addition to the traditional surface use. Almost 2 million gallons of the dispersant Corexit 9500A -- with slightly less than half released underwater -- was used to emulsify the around 5 million barrels of crude oil that poured out due to the rig explosion.

When exposed to the chemical dispersant, three species of cold-water coral showed "more severe health declines" at lower concentrations than the same species exposed to a mixture of oil and dispersant and to just oil, according to findings by scientists from Temple University and Pennsylvania State University. The oil-dispersant mixture was also more toxic than just oil, the team found.

Its study was published online in the journal *Deep-Sea Research II*.

The scientists became interested in the experiment after observing post-spill that several damaged Gulf coral populations were coated with a dark-colored wool-like slime that was found to contain oil from the spill and residues from the dispersants.

"We wanted to know if the damages that had been witnessed could have been caused by the oil, the dispersant itself, or a combination of both," Danielle DeLeo, a Temple doctoral student who was the study's lead author, said in a statement.

"We know that the corals in the Gulf were exposed to all of these different combinations, so we have been trying to determine the toxicity of the oil and the dispersants, and see what their impact would be on the corals," she said.

The corals may have a higher tolerance for the oil because they have adapted to natural seeps of oil over time in their environment, the team noted. The study also said that despite the results, "it is unclear whether short-term exposures to oil and dispersant have long-term effects," that the matter would require further study, and that long-term

oil exposure could have significant sub-lethal impacts.

"Applying the dispersants at depth was a grand experiment being conducted in real-time," Erik Cordes, an associate professor of biology at Temple, said in a statement. He has been studying Gulf of Mexico coral communities for more than a decade.

He added: "It was a desire to immediately do something about the oil coming out of the well, but they really didn't know what was going to happen as a result."

The team concluded that to improve future oil spill response efforts, "alternative methods of oil cleanup are needed and caution should be used when applying oil dispersants at depth, as it may induce further stress and damage to deep-sea ecosystems."

The study was funded by the Gulf of Mexico Research Initiative, an independent agency BP PLC funded at $500 million for 10 years in the wake of the Deepwater Horizon disaster that explores the impacts of oil spills and dispersants on local ecosystems, as well as developing improved spill mitigation, oil and gas detection, and other technologies.

Another recent study from the University of Alabama, Birmingham, found that the Corexit 9500A dispersant can damage respiratory cells of humans and animals. But a study by U.S. EPA in 2010 found the dispersant-oil combination isn't worse for shrimp, fish and other sea creatures than oil alone already is.

EPA announced a proposal to update regulations for the use of dispersants earlier this year. The plan would provide a new, well-tested and peer-reviewed laboratory method for gauging the effectiveness of products in different environments and an aquatic toxicity threshold to ensure qualifying products offer "greater performance at less environmental impact" (***Greenwire***, Jan. 13).

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**From:** Barron, Mace
**Sent:** Mon 4/13/2015 5:37:50 PM
**Subject:** Re: FYI - : BP dispersant toxic

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## OCEANS:

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effectiveness of products in different environments and an aquatic toxicity threshold to ensure qualifying products offer "greater performance at less environmental impact" (*Greenwire*, Jan. 13).

**To:** Ian P Gaudreau[ipu3@wildcats.unh.edu]
**Cc:** Mandsager, Kathy[kathy.mandsager@unh.edu]; Conmy, Robyn[Conmy.Robyn@epa.gov]; fingasmerv@shaw.ca[fingasmerv@shaw.ca]; Robert Jones - NOAA Federal[robert.jones@noaa.gov]; Samantha Joye[mandyjoye@gmail.com]; ken.lee@csiro.au[ken.lee@csiro.au]; mbleigh@alaska.edu[mbleigh@alaska.edu]; karl.linden@colorado.edu[karl.linden@colorado.edu]; kmmcfarlin@alaska.edu[kmmcfarlin@alaska.edu]; msmiles@lsu.edu[msmiles@lsu.edu]; thomas.s.coolbaugh@exxonmobil.com[thomas.s.coolbaugh@exxonmobil.com]; Mathijs.Smit@shell.com[Mathijs.Smit@shell.com]; Sprenger, Mark[Sprenger.Mark@epa.gov]; Lindsey R Howard[lrw23@wildcats.unh.edu]; nancy.kinner@unh.edu[nancy.kinner@unh.edu]; Kinner, Peter[Peter.Kinner@unh.edu]; Wilson, Gregory[Wilson.Gregory@epa.gov]; Principe, Vanessa[Principe.Vanessa@epa.gov]; tracee.nguyen@csiro.au[tracee.nguyen@csiro.au]; Ian Gaudreau[ipu3@unh.edu]; doug.helton@noaa.gov[doug.helton@noaa.gov]; Gary Shigenaka - NOAA Federal[gary.shigenaka@noaa.gov]
**From:** Hazen, Terry C (Terry)
**Sent:** Sat 4/4/2015 5:40:35 PM
**Subject:** Re: Degradation & Fate update - NEXT DISCUSSION - 3/31 at 11 ET
2015Brakstad_etal_MPB.pdf

Note the Brakstad paper is no longer in press. See attached.


**Terry C. Hazen, Ph. D.**
*UT/ORNL Governor's Chair Professor*
Department of Civil & Environmental Engineering
Department of Microbiology
Department of Earth and Planetary Sciences
Genome Science & Technology
Center for Environmental Biotechnology
Bredesen Center
The University of Tennessee
676 Dabney Hall
Knoxville, Tennessee 37996-1605
Cell: 707-631-6763
Office Phone: 865-974-7709
CEB Phone: 865-974-8080
CEB Fax: 865-974-8086
E-mail: tchazen@utk.edu
URL: http://hazenlab.utk.edu
&
Biosciences Division
Oak Ridge National Laboratory
Building 1520, Room 327, MS-6342
Oak Ridge, TN 37831-6342
Email: hazentc@ornl.gov
Phone: 865-576-8085
Fax: 865-241-1187
Cell: 707-631-6763


On Mar 31, 2015, at 7:11 PM, Ian P Gaudreau <ipu3@wildcats.unh.edu> wrote:

Hello everyone,

From today's discussion, two papers have been added to the group of papers we have been working with recently (they are also attached in this email):

Mervis 2014 (bias toward not publishing null hypothesis results)

Brakstad et al 2015 (biodegradation at low temperatures and different droplet sizes)

Ian Gaudreau

---

**From:** Mandsager, Kathy <kathy.mandsager@unh.edu>
**Sent:** Tuesday, March 31, 2015 12:24 PM
**To:** 'Conmy, Robyn'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu'; 'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; 'Mathijs.Smit@shell.com'; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** Lindsey R Howard; Kinner, Nancy; Kinner, Peter; 'wilson.gregory@epa.gov'; 'principe.vanessa@epa.gov'; 'tracee.nguyen@csiro.au'; 'Ian Gaudreau'; 'doug.helton@noaa.gov'; 'Gary Shigenaka - NOAA Federal'
**Subject:** RE: Degradation & Fate update - NEXT DISCUSSION - 3/31 at 11 ET

Attached is the paper in pdf format.

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**From:** Mandsager, Kathy
**Sent:** Tuesday, March 31, 2015 11:14 AM
**To:** 'Conmy, Robyn'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu'; 'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; 'Mathijs.Smit@shell.com'; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** 'Lindsey R Howard'; Kinner, Nancy; Kinner, Peter; 'wilson.gregory@epa.gov'; 'principe.vanessa@epa.gov'; 'tracee.nguyen@csiro.au'; 'Ian Gaudreau'; 'doug.helton@noaa.gov'; 'Gary Shigenaka - NOAA Federal'
**Subject:** RE: Degradation & Fate update - NEXT DISCUSSION - 3/31 at 11 ET

Additional paper for review. http://ac.els-cdn.com/S0025326X15000855/1-s2.0-S0025326X15000855-main.pdf?_tid=a972873c-d7b7-11e4-9464-00000aab0f27&acdnat=1427814635_2731a355cf42e8b64679699bc221613

**From:** Mandsager, Kathy
**Sent:** Monday, March 30, 2015 4:43 PM
**To:** 'Conmy, Robyn'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu'; 'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; 'Mathijs.Smit@shell.com'; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** 'Lindsey R Howard'; Kinner, Nancy; Kinner, Peter; 'wilson.gregory@epa.gov'; 'principe.vanessa@epa.gov'; 'tracee.nguyen@csiro.au'; 'Ian Gaudreau'; 'doug.helton@noaa.gov'; 'Gary Shigenaka - NOAA Federal'; Mandsager, Kathy
**Subject:** RE: Degradation & Fate update - NEXT DISCUSSION - 3/31 at 11 ET

This is a reminder of our WebEx meeting tomorrow.

**From:** Mandsager, Kathy
**Sent:** Friday, March 20, 2015 6:19 PM
**To:** 'Conmy, Robyn'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu'; 'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; 'Mathijs.Smit@shell.com'; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** 'Lindsey R Howard'; Kinner, Nancy; Kinner, Peter; 'wilson.gregory@epa.gov'; 'principe.vanessa@epa.gov'; 'tracee.nguyen@csiro.au'; 'Ian Gaudreau'; 'doug.helton@noaa.gov'; 'Gary Shigenaka - NOAA Federal'
**Subject:** RE: Degradation & Fate update - NEXT DISCUSSION - 3/31 at 11 ET

Mark your calendar! This is to confirm our next meeting for **Tuesday, March 31** beginning at 11:00 am ET.
Her are the WebEx directions to join this meeting. Thank you!

## Degradation & Fate Group

Tuesday, March 31, 2015

11:00 am | Eastern Daylight Time (New York, GMT-04:00) | 2 hrs

Join WebEx meeting

Meeting number: 734 916 289

## Join by phone

**1-855-244-8681** Call-in toll-free number (US/Canada)

**1-650-479-3207** Call-in toll number (US/Canada)

Access code: 734 916 289

Global call-in numbers | Toll-free calling restrictions

Can't join the meeting? Contact support.

**From:** Mandsager, Kathy
**Sent:** Thursday, March 19, 2015 8:31 AM
**To:** 'Conmy, Robyn'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu'; 'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; 'Mathijs.Smit@shell.com'; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** 'Lindsey R Howard'; Kinner, Nancy; Kinner, Peter; 'wilson.gregory@epa.gov'; 'principe.vanessa@epa.gov'; 'tracee.nguyen@csiro.au'; 'Ian Gaudreau'; 'doug.helton@noaa.gov'; 'Gary Shigenaka - NOAA Federal'
**Subject:** RE: Degradation & Fate update - NEXT DISCUSSION

I greatly appreciate your patience with this process. Please **cancel** the tentative hold on your calendar for tomorrow 3/20. Since we would greatly appreciate a majority of this group to participate in this 2-hour WebEx meeting, I am making another attempt at scheduling this call. Please use this doodle poll (all times noted are ET). Thank you to each of you!

Doodle poll here>> http://doodle.com/2w3gyb3gv4sv7iek

**From:** Mandsager, Kathy
**Sent:** Monday, March 16, 2015 4:39 PM
**To:** 'Conmy, Robyn'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu'; 'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; 'Mathijs.Smit@shell.com'; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** 'Lindsey R Howard'; Kinner, Nancy; Kinner, Peter; 'wilson.gregory@epa.gov'; 'principe.vanessa@epa.gov'; 'tracee.nguyen@csiro.au'; 'Ian Gaudreau'
**Subject:** RE: Degradation & Fate update - NEXT DISCUSSION

In the spirit of trying to keep everyone informed – there will NOT be a meeting tomorrow at 2 (see request below). I was unable to gain a quorum. Please continue to hold this Friday 3/20 as a potential meeting time. And if you have not yet responded with your availability, please let me know if you could possibly make in on **3/20 beginning at 1pm ET.**
Thank you.

**From:** Mandsager, Kathy
**Sent:** Monday, March 16, 2015 9:38 AM
**To:** 'Ian P Gaudreau'; 'Conmy, Robyn'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu'; 'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; 'Mathijs.Smit@shell.com'; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** 'Lindsey R Howard'; Kinner, Nancy; Kinner, Peter; 'wilson.gregory@epa.gov'; 'principe.vanessa@epa.gov'; 'tracee.nguyen@csiro.au'; 'Ian Gaudreau'
**Subject:** RE: Degradation & Fate update - NEXT DISCUSSION
**Importance:** High

While these papers are fresh on your mind, I am offering some dates as soon as possible for our next meeting. Kindly let me know if you can make yourself available for about a 2-hour timeslot at any of the following times:

Tuesday (tomorrow) 3/17 beginning at 2:00 pm ET
Friday 3/20 beginning at 12noon ET
Friday 3/20 beginning at 1:00 pm ET
Friday 3/20 beginning at 2:00 pm ET
Friday 3/20 beginning at 3:00 pm ET
Thursday 3/26 at 10:00 am ET
Monday 3/30 beginning at 2:20 pm ET

A speedy reply will be greatly appreciated. Thank you!

**From:** Ian P Gaudreau [mailto:ipu3@wildcats.unh.edu]
**Sent:** Friday, March 13, 2015 10:16 AM
**To:** 'Conmy, Robyn'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu'; 'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; 'Mathijs.Smit@shell.com'; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** Lindsey R Howard; Mandsager, Kathy; Kinner, Nancy; Kinner, Peter; 'wilson.gregory@epa.gov'; 'principe.vanessa@epa.gov'; tracee.nguyen@csiro.au; Ian Gaudreau
**Subject:** Degradation & Fate update - Official Papers

Hi folks,

Thank you for hanging in there on the conference call Wednesday. We really appreciate all of the hard work you have been doing. The 13 official papers you decided you would review and use as the basis for your comments (e.g. knowns, uncertainties) on the effect of chemical dispersants on oil biodegradation are:

- Venosa & Holder 2007
- Prince et al. 2013
- Prince & Butler 2014
- Mcnaughton et al. 2003
- McFarlin et al. 2014

- Mason et al. 2012
- Lindstrom & Braddock 2002
- Kleindienst et al. 2015
- Chakroborty et al. 2012
- Campo et al. 2013
- Bruheim et al. 1997
- Bruheum et al. 1999
- Baelum et al. 2012

These papers are all located in a folder on BOX entitled "Papers selected by panel - Effect of Chemical Dispersants on Oil Biodegradation". This link can be found here: https://unh.app.box.com/files/0/f/3252405678/Papers_selected_by_panel_-_Effect_of_Chemical_Dispersants_on_Oil_Biodegradation

Kathy will be contacting you to schedule what will hopefully be our final meeting of the Degradation & Fate group.

In preparation for the meeting, please re-read the paper and if you have time, send Kathy the conclusions that you derive from these references regarding what is known and uncertain about the effect of chemical dispersants on the biodegradation of oil, particularly as it applies to the Arctic.

Also, we need your feedback on a paper by Harris et al. 2002 (paper is attached in this email). Would you like us to add this paper to the "Papers selected by panel - Effect of Chemical Dispersants on Oil Biodegradation" folder on BOX? Here is the citation:

Harris, B.C. et al. 2002. Nutrient effects on the biodegradation rates of chemically-dispersed crude oil. *In* Twenty-Fifth Arctic and Marine Oilspill Program (AMOP) Technical Seminar, Nineteenth Technical Seminar on Chemical Spills (TSOCS) and Fourth Biotechnology Solutions for Spills (BIOSS): June 11 to 13, 2002, Westin Calgary Hotel, Calgary, Alberta, Canada: Proceedings. Ottawa, Ont.: Environment Canada. pp. 877-893.

Thanks again for your time and energy. I look forward to talking with you again.

Nancy E. Kinner, Ph.D.
University Professor
Professor Civil/Environmental Engineering
UNH Director, Coastal Response Research Center
Director, Center for Spills in the Environment
236 Gregg Hall
University of New Hampshire
Durham, NH 03824
Phone: 603-862-1422
Fax: 603-862-3957
http://www.crrc.unh.edu

<Brakstad et al 2015.pdf><Mervis 2014.pdf>

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# Biodegradation of dispersed Macondo oil in seawater at low temperature and different oil droplet sizes

Odd G. Brakstad ⇑, Trond Nordtug, Mimmi Throne-Holst

SINTEF Materials and Chemistry, Environmental Technology, Dept. Applied Environmental Biology and Chemistry, N-7465 Trondheim, Norway

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abstract

During the Deepwater Horizon (DWH) accident in 2010 a dispersant (Corexit 9500) was applied at the wellhead to disperse the Macondo oil and reduce the formation of surface slicks. A subsurface plume of small oil droplets was generated near the leaking well at 900–1300 m depth. A novel laboratory system was established to investigate biodegradation of small droplet oil dispersions (10 l m or 30 l m droplet sizes) of the Macondo oil premixed with Corexit 9500, using coastal Norwegian seawater at a temperature similar to the DWH plume (4–5 ffC). Biotransformation of volatile and semivolatile hydrocarbons and oil compound groups was generally faster in the 10 l m than in the 30 l m dispersions, showing the importance of oil droplet size for biodegradation. These data therefore indicated that dispersant treatment to reduce the oil droplet size may increase the biodegradation rates of oil compounds in the deepwater oil droplets.

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## 1. Introduction

During the Deepwater Horizon (DWH) incident some of the oil was dispersed as small droplets in the deep ocean at depths of 900–1300 m near the leaking well, and at water temperatures of 4–6 ffC (Camilli et al., 2010; Reddy et al., 2012). Simulations of the plume trajectories predicted that oil droplets with diameters between 10 and 50 l m would form in a distinct subsurface layer and be transported horizontally, while droplets larger than 90 l m rapidly rose to the surface (North et al., 2011). Samples from the deepwater plume showed enrichment of water-soluble components (Camilli et al., 2010). Measurements of PAH in water samples during the release showed rapid decrease with distance from the release point. The responders began injecting the chemical dispersant Corexit 9500A at the wellhead in early May 2010 to reduce the amount of oil that formed surface slicks and reached the Gulf of Mexico (GoM) coastlines (Atlas and Hazen, 2011; Kujawinski et al., 2011). In addition, surface operations included mechanical recovery techniques and application of the chemical dispersants Corexit 9527 and 9500A (Coastal Response Research Center, 2010).

It was early observed that the deepwater plume stimulated bacteria associated with hydrocarbon biodegradation in cold seawater (Oceanospirillaceae, Pseudomonas, Cycloclasticus, Colwellia, Pseudoalteromonas, Methylophaga) (Valentine et al., 2010; Hazen et al., 2010; Redmond and Valentine, 2012; Dubinsky et al., 2013), and data from the field and from laboratory experiments indicated short biodegradation half-lives for $nC_{13}$–$nC_{26}$ alkanes, ranging from 1 to 8 days (Hazen et al., 2010). A sequential and pulsed propagation of bacteria degrading specific hydrocarbons was suggested, including n-alkanes, aromatics and $C_1$–$C_3$ gas components (Valentine et al., 2012; Dubinsky et al., 2013). Results from stable isotope analyses reported that close to 70% of the oxygen consumption in the deepwater plume was related to bacterial respiration of propane and ethane (Valentine et al., 2010), while methane oxidation was delayed (Valentine et al., 2010; Kessler et al., 2011).

Biodegradation rates of components in dispersed oil are normally expected to increase when oil droplet size is reduced, for instance by treatment of the oil with chemical dispersants. Smaller droplets will generate larger oil–water interphase areas for the oil-degrading bacteria to attach to, and dissolution of water-soluble compounds will increase. Volatile oil compounds will rapidly dissolve during subsurface spills and thereby become subject to biodegradation. In contrast volatiles will largely evaporate after surface spills. Several laboratory studies have shown that dispersant treatment of dispersible oils increase oil compound biodegradation (Siron et al., 1995; Venosa and Holder, 2007; Prince et al., 2013; McFarlin et al., 2014; Brakstad et al., 2014).

To our knowledge, no laboratory studies have attempted to relate the biodegradation of oil compounds to measured droplet sizes in the dispersions. We therefore established a novel

⇑ Corresponding author. Tel.: +47 98243447; fax: +47 73597043.
E-mail address: odd.brakstad@sintef.no (O.G. Brakstad).

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experimental system for comparing oil dispersions of different small droplet sizes in natural seawater. This system was based on combining an oil dispersion generator (Nordtug et al., 2011) and a slowly rotating carousel system to generate small droplet dispersions and avoid droplets rising to the surface. The primary aim of our study was therefore to quantify biodegradation of hydrocarbons in dispersions with defined oil droplet sizes relevant for chemically dispersed oil, and at low seawater temperatures, corresponding to deepwater discharges. Biodegradation of chemically dispersed Macondo oil at two median oil droplet sizes (10 and 30 lm) in natural seawater at 4–5 ffC was investigated with this system. Norwegian coastal seawater was used in the study, but experimental conditions (oil, oil droplet size distributions and seawater temperature) were relevant to the DWH deepwater plume.

## 2. Materials and methods

### 2.1. Oil, dispersant and seawater used in experiments

Unweathered Macondo (MASS) oil was collected from a riser pipe connected to the well on 22 May 2010. COREXIT 9500A (Nalco, Sugar Land, TX) dispersant was used at a dispersant-to-oil ratio (DOR) of 1:100. Seawater was collected from a depth of 80 m (below thermocline) in a Norwegian fjord (Trondheimsfjord; 63ff26°N, 10ff23°E), outside the harbor area of Trondheim, the water is supplied via a pipeline system to our laboratories. The water source is considered to be non-polluted and not influenced by seasonal variations. The salinity of the seawater was 34‰, with a water temperature of 6–8 ffC and dissolved oxygen (DO) of approximately 8 mg/L when reaching our laboratory (Brakstad et al., 2004).

### 2.2. Oil dispersion generator and carousel system

An oil droplet generator was used for preparing oil dispersions with defined droplet size distributions, as previously described (Nordtug et al., 2011). The system consists of 3 chambers with an inner diameter of 8 mm connected by nozzles with a diameter of 0.5 mm. Oil dispersions with defined oil droplet size distributions and concentrations are generated by injecting oil via a capillary into a flow of seawater which moves through the chambers (Nordtug et al., 2011). Oil droplet concentrations and size distribution were determined by Coulter Counter analyses (see below). Flasks (2 L; Schott) were baked (450 ffC; 3 h) and soaked overnight (4% Deconex 11 Universal, Borer, Switzerland), washed with detergent (Neodisher N, Dr. Weigert, Germany), and thoroughly rinsed and autoclaved (121 ffC, 20 min) before use.

The flasks were completely filled with oil dispersions (no headspace or air bubbles) and mounted on a carousel system. During mounting of flasks and biodegradation experiments the wheels were slowly rotated around the carousel axis (0.75 r.p.m.) by a gear motor (SEW Eurodrive, Moss, Norway). In the main biodegradation experiment described here, four carousels with double sets of wheels, holding up to 16 flasks each, were used.

### 2.3. Biodegradation experiment

The MASS oil was heated at 50 ffC for 30 min, mixed by shaking for 3 min, and cooled to room temperature, after which it was mixed with the dispersant Corexit 9500A (DOR 1:100) at room temperature. This dispersant was shown to effectively disperse the Macondo oil (Daling et al., 2014). Pre-adaption of the seawater prior to the biodegradation experiments was conducted by diluting a stock dispersion (200 mg/L oil; oil droplet size 10 lm) to 0.2 mg/L Macondo oil (measured by Coulter Counter) in natural unfiltered seawater (pre-incubated over night at 5 ffC) in 2-L flasks completely filled (no air bubbles) with the dispersions, with incubation in the carousel system at 5 ffC for 5 days (rotation 0.75 r.p.m.). The experiment was then started by generating dispersions in the pre-adapted seawater with median oil droplet sizes of 10 lm or 30 lm and nominal oil concentration of 2 mg/L from a stock oil dispersion (200 mg/L oil) in natural unfiltered seawater. Dispersions of 10 lm or 30 lm median oil droplet sizes and 2 mg/L nominal concentrations were also prepared in sterile-filtered (0.2 lm) seawater (incubated at 4–5 ffC overnight before use) supplemented with $HgCl_2$ (100 mg/L), to minimize bacterial growth. Immediately after generation of dispersions flask were mounted on the carousel at slow rotation (0.75 r.p.m.). Flasks with experimental blank samples (unfiltered seawater without oil) were also included in the experiment for background analyses. Experiments were conducted at 5 ffC for up to 64 days. Flasks (triplicate samples; 2.3 L sample) of dispersions in natural seawater were sacrificed for analyses after 15 min on the carousel (0-day samples) and after 2, 4, 8, 16, 32, or 64 days of incubation on the carousels. One sterilized control flask and one experimental blank flask were also sacrificed for analyses at the each sampling point.

### 2.4. Analyses

#### 2.4.1. Oil droplet analyses

Oil droplet concentrations and size distributions were determined by Coulter Counter measure (Beckman Multisizer 4; Beckman Coulter Inc., Brea, CA, USA) fitted with either 100 lm or 280 lm apertures, for measurement of droplets within a diameter range of 2–60 lm or 5.6–100 lm, respectively. Filtered (0.22 lm) seawater was used as electrolyte. All median droplet sizes reported here are expressed as median droplets diameter on droplet volume if not otherwise mentioned.

#### 2.4.2. Chemical analyses

Samples of dispersions and seawater were solvent–solvent extracted with dichloromethane (DCM) for measurements of semivolatile organic compounds (SVOC) by gas chromatographic methods. The flask glass walls were also rinsed with DCM after removal of dispersions to extract material attached to the glass walls. All extracts were pooled before analyses. A gas chromatograph coupled to a flame ionization detector (GC-FID; Agilent 6890 N with 30 mDB1 column; Agilent Technologies) was used for quantification of extracted $C_{10}$–$C_{36}$ saturates separated according to boiling points, termed as total petroleum hydrocarbons extractable organic carbon (TEOC), while 96 individual targeted compounds ($C_{10}$–$C_{36}$ n-alkanes, decalines, phenols, 2- to 5-ring polyaromatic hydrocarbons (PAH) and 17a(H),21b(H)-Hopane (30ab Hopane) were analyzed in a gas chromatograph coupled to a mass spectrometer (GC–MS; Agilent 6890 plus GC coupled with an Agilent 5973 MSD detector, operated in Selected Ion Monitoring [SIM] modus; Agilent Technologies), as recently described (Brakstad et al., 2014). Dispersions were acidified (pH < 2) for analyses of 87 targeted volatile organic carbon (VOC) compounds in a Purge & Trap unit (Teledyne Tekmar Atomx; Mason OH, USA.) coupled to a GC–MS (Agilent 6890 N GC and an Agilent 5975B MSD detector; Agilent Technologies)(P&T GC–MS). The VOC and SVOC target compounds included in GC–MS analyses are shown in Table S1. The response values for individual target analytes were determined, with a signal-to-noise ratio of 10 as the lower detection limit, and a lower limit of detection (LOD) of 0.01 lg/L was defined for individual oil compounds.

#### 2.4.3. Temperature, dissolved oxygen, nutrients, and biomass

Air and seawater temperatures were logged through the experimental period. Dissolved oxygen was measured by a

dissolved oxygen meter (YSI, Inc., Yellow Springs, OH). Nutrient analyses included $NO_3$–N + $NO_2$–N (ISO 13395), $NH_4$–N (ISO 11732), o-$PO_4$–P (ISO 15681-2), and total Phosphorous (ISO 15681-2), analyzed by Eurofins Environment Testing Norway, Bergen, Norway. Microbial biomass concentrations were determined by epifluorescence microcopy analyses of samples stained by the nucleic acid stain 4°,6-diamidino-2-phenylindol (Porter and Feig, 1980).

### 2.5. Calculations and statistics

Non-linear regression analyses were performed by a 1st order rate approach with determination of lag-phases included using the option "plateau followed by one-phase decay" in GraphPad Prism vs. 6.0 (GraphPad Software Inc., La Jolla, CA, USA). Rate coefficients (k1) were determined for the decay-period, the plateau period defined the lag-phase, and half-lives were determined from rate coefficients and plateau periods (t1/2 = plateau period + 0.693/k1). Rate data were determined for both single oil components and for 22 oil compound groups described in the Oil-Spill Contingency and Response model OSCAR (Reed et al., 2000). The group composition is described in Table S1.

Column statistics were compared by Wilcoxon matched paired test in GraphPad Prism vs. 6.

## 3. Results and discussion

### 3.1. Generation and maintenance of oil dispersions over time

Dispersions of Macondo oil mixed with Corexit 9500A (DOR of 1:100) were generated by different seawater flow-rates through the oil droplet generator system, from 50 to 150 ml/min. This resulted in oil dispersions with median droplet size distributions of approximately 10 l m to 30 l m in diameter (Fig. 1). The oil pump of the dispersion generator was set to generate fixed nominal oil concentrations during the dispersion generation (0.2–200 mg oil per L of water), and good agreement between nominal oil concentrations and measured oil droplet concentrations was recorded (data not shown). Recent studies have shown that nearly the same oil droplet size distribution is generated in this system both with and without premixing of oil with chemical dispersant (Nordtug et al., 2011).

The carousel system was developed for maintaining the droplet size distribution in the oil dispersions while incubating the dispersions over time. All experiments in the carousels were conducted in air-tight flasks without headspace to avoid evaporative depletion. The system was able to handle dispersions of fresh Macondo oil with small droplets, in the diameter size range of 10–30 l m, with rising velocities of 1.6–14.4 cm/h, according to Stoke's law. We believe the ability of keeping the droplets in suspension is due to the combined effect of the turbulence created in the flasks and the fact that the oil droplet rising velocities will make them constantly change direction in relation to any fixed point at the flasks inner surface. Larger than 30 l m oil droplets resulted in inhomogeneous dispersions during transfer from dispersion generator to flasks in carousel system because of elevated rising velocities. In initial experiments with 10 l m median volumetric droplet dispersions in a sterilized system (filtered seawater poisoned with $HgCl_2$), the droplet sizes were maintained for at least 28 days in the carousel system, while measured droplet concentration decreased (see Supplementary Information, Fig. S1).

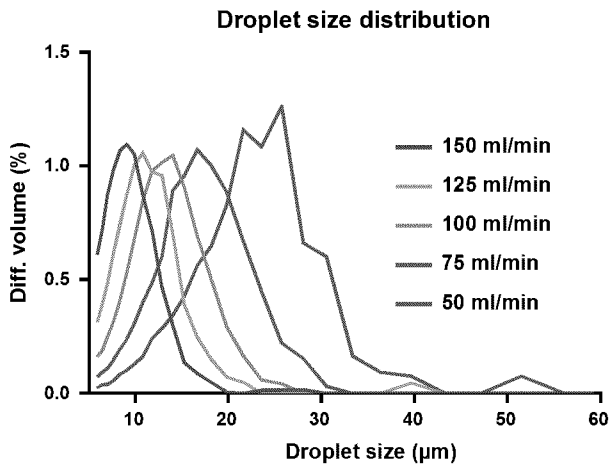


Fig. 1. Average oil droplet size distributions generated in the oil dispersion generator at different seawater flow-rates after premixing of the oil with Corexit 9500A.

### 3.2. Biodegradation experiment with two dispersions of different oil droplet size distributions

An oil dispersion biodegradation experiment was performed at 5 fC (64 days) with nominal oil concentrations of 2 mg/L generated in the dispersion generator at median oil droplet sizes on volume of 10 l m and 30 l m in diameter, and with natural seawater pre-adapted to the oil and temperature (see Section 2). The low oil concentration used in this experiment is consistent with recent recommendations to avoid too high oil loading during biodegradation studies of dispersed oil (Lee et al., 2013). Seawater pre-adaption was included since many offshore oil production areas may be exposed to hydrocarbons through natural seepage or produced water releases. For instance, a recent hydrocarbon seepage flux of 2.2–18 ┐ $10^7$ tons per year has been estimated for the GoM region, corresponding to 14–120% of the DWH discharge rate (Smith et al., 2014). Analyses of macronutrients ($NO_3$ + N $O_2$–N, $NH_4$–N and o-$PO_4$–P) and dissolved oxygen showed no apparent limitations in oxygen or inorganic nutrient levels during the biodegradation experiment (Supplementary Information, Figs. S2 and S3).

#### 3.2.1. Oil droplet sizes and concentrations

The oil droplet size distributions and concentrations were followed in the dispersions during the biodegradation experiment (Fig. 2). Results from Coulter Counter analyses showed that the initial median oil droplet size distributions in the 10 l m and 30 l m dispersions were 11.0 ± 0.04 l m and 29.4 ± 3.5 l m, and that the 10 l m and 30 l m dispersions represented oil surfaces of 10.9 ± 0.2 ┐ $10^5$ and 5.4 ± 0.9 ┐ $10^5$ l $m^2$/ml, respectively. The dispersions with the smaller droplets therefore contained approximately twice the surface area of the dispersions with the larger droplet. Assuming a microbial size of 1 l m in diameter and the maximum microbial density of 1 cell/l $m^2$ of oil droplet surface area (Horowitz et al., 1975; Vilcaez et al., 2013) the initial oil droplet concentrations represented sufficient surface areas for colonization of up 10 ┐ $10^5$ cells/ml in the 10 l m dispersions and 5 ┐ $10^5$ cells/ml in the 30 l m dispersions. Initial cell concentrations determined by epifluorescence microscopy were 8 ┐ $10^5$ and 12 ┐ $10^5$ cells/ml in the 10 l m and 30 l m dispersions, respectively. The oil droplets therefore represented surface areas for attachment of the entire bacterial population in the 10 l m dispersions and approximately 40% of the population in the 30 l m dispersions at the start of the experiment.

The oil droplet size distributions during the biodegradation period (Fig. 2A) were maintained in the 10 l m dispersions (average median droplet size of 3 replicates ranging from 10.7 to 13.4 l m in the natural unfiltered seawater and 8.5–11.1 l m in sterile dispersions). However, the 30 l m dispersions in natural

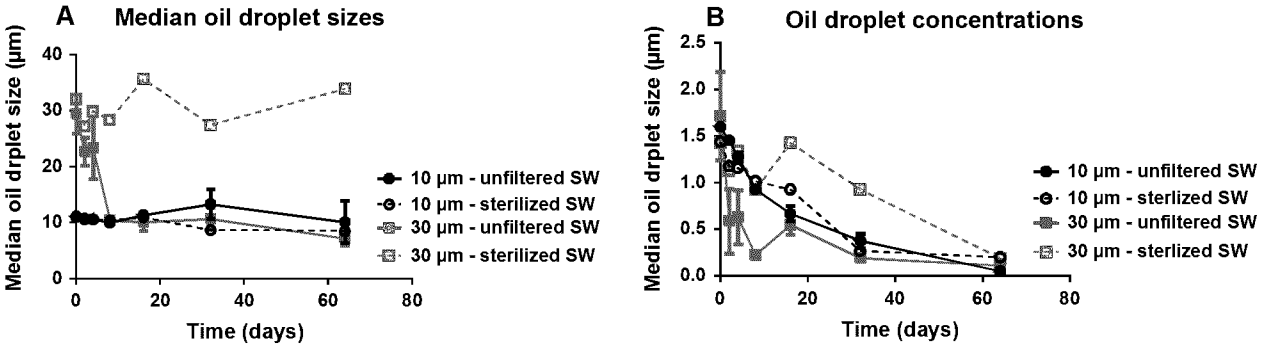


Fig. 2. Median oil droplet sizes (A) and concentrations (B) in oil dispersions generated during a biodegradation period of 64 days at 5 fC in natural unfiltered seawater (unfiltered SW), or in filtered (0.1 l m) and sterilized ($HgCl_2$) seawater (sterilized SW). The dispersions were generated at nominal particle sizes of 10 and 30 l m diameter. The dispersions in unfiltered seawater were analyzed in triplicate (error bars show standard deviation), while sterile samples were analyzed as single samples.

seawater experienced a rapid decline in droplet size between days 0 and 8, from 29.4 to 10.4 l m in average diameter (3 replicates), with a subsequent particle size between 10.2 and 13.4 l m median in the period from day 8 to 64. In contrast, the median oil droplet diameter was maintained in the sterile 30 l m dispersions, ranging from 27.2 to 34.9 l m during the experimental period (Fig. 2A). When oil droplet concentrations were determined by Coulter Counter analyses the concentrations declined more rapidly in natural unfiltered seawater than in the sterilized dispersions. In the 10 l m dispersions the concentrations were decreased from days 0 to 8 by 41.9% (from 1.60 to 0.93 mg/L average values) in natural unfiltered seawater and by 29.2% (from 1.44 to 1.02 mg/L) in the sterilized dispersions, while the reductions in the 30 l m dispersions were 86.9% (from 1.72 mg/L to 0.22 mg/L) and 35.0% (from 1.43 mg/L to 0.93 mg/L) in unfiltered and sterilized seawater, respectively (Fig. 2B). In the sterilized systems with 30 l m oil droplets it was evident that the larger droplets were removed faster than the smaller droplets (Supplementary Information, Fig. S4D). Reduced concentrations of droplets may therefore be caused by removal of the larger droplets with the fastest rising velocities or by droplet coalescence, generating droplets of sizes outside the measuring range of the Coulter Counter instrument (5.6–100 l m), as shown in oil droplet coalescence models (Sterling et al., 2004). The 10 l m dispersions also included oil droplets smaller than the lower instrumental measuring size of 5.6 l m (Supplementary Information, Figs. S4A and S4B). In addition, oil droplets could be removed from the system by attachment to the glass walls of the flasks, as measured by chemical analyses (see below). The higher reduction in oil droplet concentrations in unfiltered than sterilized dispersions may be caused by integration of droplets in "clusters" or "flocs" in natural seawater, which were visually observed in the experiment. These aggregates have been observed in several biodegradation studies of dispersed oil (e.g. Swannell et al., 1997; Harris et al., 2002; MacNaughton et al., 2003; Bælum et al., 2012).

### 3.2.2. Biodegradation of targeted oil compounds

Concentrations of 183 targeted semivolatile or volatile oil compound measured by GC–MS analyses showed that 81.4% of these were detected in the dispersions above the LOD (0.01 l g/L) at the start of the experiment. Compounds not detected above LOD included $C_0$–$C_4$ phenols and benzothiophenes (Supplementary Information, Fig. S5), while additional 13 compounds (7.1%) with concentrations close to LOD (60.1 l g/L) were excluded for biodegradation determination (Supplementary Information, Fig. S5).

Depletion of semivolatile $nC_{10}$–$nC_{36}$ alkanes and non-alkylated and alkyl-substituted decalines, naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, fluoranthenes and chrysenes were examined in the dispersions after normalization against the persistent biomarker 17a(H),21b(H)-Hopane (30ab Hopane), commonly used in biodegradation studies (Prince et al., 1994; Page et al., 1995; Wang et al., 1998). The depletions were determined as percentages of normalized data at the start of the experiment (day 0) for each target oil compound (Fig. 3). In average, the oil compound groups showed low to negligible depletion in sterilized dispersions during the first 32 days (average <1%), although decaline concentrations were reduced by more than 20%. After 64 days the oil compounds were further depleted in the sterilized dispersions (average reduction of 19%). However, compounds in natural unfiltered seawater were mostly reduced to near completion before they were depleted in the sterilized dispersions. The oil compound depletion in natural unfiltered seawater was therefore mainly the result of biotransformation.

Low-range ($nC_{10}$–$nC_{15}$) and medium-range ($nC_{16}$–$nC_{21}$) molecular weight (MW) n-alkanes were rapidly biotransformed after 4 days in the 10 l m dispersions (76.3 ± 2.7 and 74.5 ± 1.9% depletion, respectively), while biotransformation of these n-alkanes started later in the 30 l m dispersions and did not become evident until 8 days (84.2 ± 4.6 and 82.2 ± 3.4% degradation, respectively) in the 30 l m dispersions (Fig. 3A). Faster biotransformation of the low-range and medium-range MW n-alkanes was therefore measured in the 10 l m than the 30 l m dispersions. Also decaline biotransformation started faster in the smaller droplet dispersions, between days 8 and 16 in 10 l m dispersions (60.6 ± 3.6% degradation), and between days 16 and 32 (88.7 ± 9.5% degradation at 32 days) in the 30 l m dispersions (Fig. 3A). However, high-range MW n-alkanes ($nC_{22}$–$nC_{36}$) shower slower and more similar biotransformation in the two dispersions (73.0 ± 4.8 and 63.5 ± 0.5% degradation in the 10 l m and 30 l m dispersions after 16 days)(Fig. 3A).

Low-range and medium-range MW PAH-compounds (2- to 3-ring PAH) were biotransformed between day 8 and 16 in both dispersions, with 99.7 ± 0.2 and 88.9 ± 9.0% degradation after 16 days in the 10 and 30 l m dispersions, respectively (Fig. 3B). Also for these PAH compounds faster biodegradation in the 10 l m than the 30 l m oil droplet dispersions was indicated. However, larger PAH (4- to 5-ring) were only biotransformed between 32 and 64 days, with 95.7 ± 5.2 and 88.7 ± 2.1% decay in the 10 and 30 l m dispersions after 64 days.

VOC compounds determined by P&T GC–MS analyses could not be normalized against a biomarker, since analyses of these did not include any recalcitrant biomarker. Determination of % concentrations relative to 0-day concentrations for the alkane and aromatic VOC compound groups showed biotransformation mainly between 8 and 16 days, resulting in 99.6 ± 0.05 and 96.5 ± 5.0% depletion of

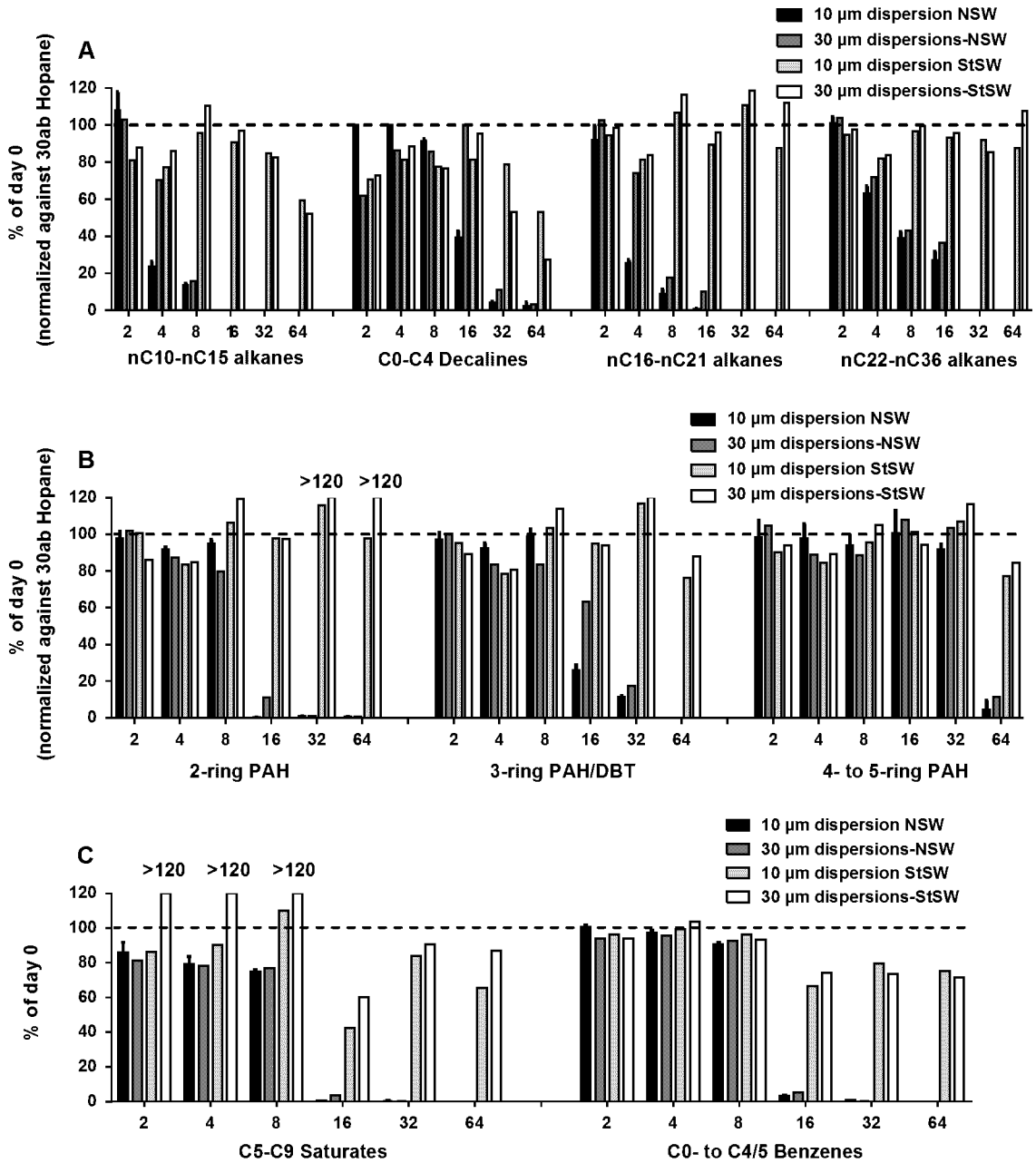


Fig. 3. Percentage concentrations compared to day 0 of semivolatile n-alkanes and $C_0$–$C_4$ alkylated decalines (A), semivolatile 2–5 ring PAH (B), and volatile alkanes and aromatic hydrocarbons (C) in 10 l m and 30 l m dispersions in natural seawater (NSW) and sterilized seawater (StSW) during an incubation period of 64 days, with samples collected after 2, 4, 8, 16, 32 and 64 days. The percentages of semivolatile compounds were determined from GC–MS analyses (triplicate) normalized against the biomarker 30ab Hopane with standard deviation error bars of 3 replicates. Volatile compounds were determined without normalization. The broken line shows the 0-day 100% for each target compound.

$C_5$–$C_9$ alkanes in 10 l m and 30 l m dispersions, respectively, while corresponding data for $C_0$- to $C_4$/$C_5$ benzenes were 96.8 ± 0.5 and 94.4 ± 2.3% depletion (Fig. 3C). Although sterilized dispersions also showed decreased concentrations of volatiles after 16 days (39.7–57.7% and 25.9–33.5% depletion of saturates and benzenes, respectively) most of the depletion in natural unfiltered seawater may therefore be accounted for by biodegradation.

Non-linear regression analyses of single oil compounds (normalized against 30ab Hopane) were performed by 1st order rate kinetics not including the determined lag-phases, and rate coefficients and half-lives for targeted oil compounds were determined in the dispersions. Low oil concentrations with no significant increase in microbial concentrations (epifluorescence microscopy) during the biodegradation period (average cell numbers differed with a factor of 1.02 between days 0 and 64) argued for 1st order kinetics to determine biotransformation coefficients and half-lives (Battersby, 1990). Non-responsive periods (lag-phases) were observed for most of the targeted compounds (Fig. 3). During the DWH spill it was suggested that deepwater with bacteria re-entered the spill site and caused accelerated hydrocarbon biodegradation (Valentine et al., 2012), resulting in a situation in which hydrocarbon-stimulated bacterial populations eventually could degrade oil compounds without a preceding lag-phase.

First-order rate calculations of targeted semivolatile n-alkanes and 2- to 4-ring PAH normalized against 30ab Hopane were performed (Fig. 4, Table S2). Half-lives calculated from the rate

coefficients varied from 0.6–5.6 days (median 1.1 days) and 1.1–11.1 days (median 2.5 days) for $nC_{10}$–$nC_{30}$ alkanes in 10 l m and 30 l m dispersions, respectively, while corresponding data for 2- to 4-ring PAH were 0.9–31.9 (median 5.3 days) and 0.9–54.9 days (median 10.2 days). The half-lives for most of the targeted compounds (44 of 48 compounds) were lower in the 10 l m than the 30 l m dispersions, and the differences between the dispersions were significant ($P < 0.05$; Wilcoxon non-parametric t-test). The n-alkane half-lives were increased with longer carbon-chains in both dispersions, primarily in the high-boiling-point range (P $nC_{21}$). PAH half-lives increased in both dispersions with increasing numbers of aromatic rings and with degree of alkyl-substitution, except for the chrysenes (Fig. 4). Only small differences in half-lives were determined for chrysenes, which appeared in low concentrations in the dispersions (sum of $C_0$–$C_4$ chrysenes of 0.59 and 0.79 l g/L in 10 l m and 30 l m dispersions, respectively; supplementary information Fig. S5). Small oil droplets therefore had a positive impact on biotransformation of both n-alkanes and PAH. In a recent study of Macondo oil biodegradation under a near-surface temperature relevant for the GoM, comparing physically and chemically dispersed oil, we observed higher biodegradation differences related to droplet size for n-alkanes ($nC_{10}$–$nC_{30}$) than 2- to 4-ring PAH (Brakstad et al., 2014). However, in the near-surface oil biodegradation study both temperature (30–32 fC), experimental system and oil droplet size distributions differed from the current experiment. The different temperatures will also stimulate different taxa of oil-degrading bacteria, as shown from field analyses of the DWH incident, in which none of the predominant bacteria in the deepwater plume (Oceanospirillales, Colwellia and Cycloclasticus) were abundant in surface slicks (Redmond and Valentine, 2012). Detailed results from characterization of cell counts and bacterial communities from the current study will be presented in a separate manuscript (Brakstad et al., in preparation). And importantly, the oil characteristics will be different at the two temperatures. For instance some of the larger n-alkanes may generate wax crystals at low temperature, thereby becoming less susceptible to biodegradation.

First-order rates are often calculated without accounting for the lag-phases. In these studies the lag-periods become a part of the half-live determination. In Table S2 (Supplementary Information) the half-lives are also determined as the sum of the lag-periods and the half-lives determined from the rate coefficients. By these calculations the n-alkane half-lives varied from 2–17.6 days in the 10 l m dispersions and 3.1–20.8 days in the 30 l m dispersions. PAH half-lives varied correspondently from 8.8–49.9 and 8.7–79.9 days in the two dispersions. The same trends for n-alkanes and PAH were observed with these half-life calculations as described above, with generally shorter half-lives of the same compounds in the 10 l m than in the 30 l m dispersions. The sums of half-lives and lag-phases also differed significantly between the 10 l m and the 30 l m dispersions ($P < 0.05$; Wilcoxon non-parametric t-test).

Our n-alkane and PAH biodegradation data, using coastal Norwegian seawater from 80 m depth, mainly coincided with results from studies with chemically dispersed oils incubated at low temperature (└1 to +8 fC), in which n-alkane depletion corresponded to half-lives of 2 to approximately 10 days, while 2- to 4-ring half-lives ranged between 2 and 37 days (Siron et al., 1995; Venosa and Holder, 2007; Prince et al., 2013; McFarlin et al., 2014). Also results from the DWH deepwater plume samples and laboratory studies with microbial consortia or seawater from GoM indicated average n-alkane ($nC_{13}$-$nC_{26}$) half-lives of 1.2–6.1 days (Hazen et al., 2010), showing good agreement with our results. In a recent study with small droplet (10–30 l m) dispersions of Macondo oil in GoM deepwater, biotransformation of 2–3 ring PAH appeared mainly between 9 and 39 days of incubation, while 4–6 ring PAH

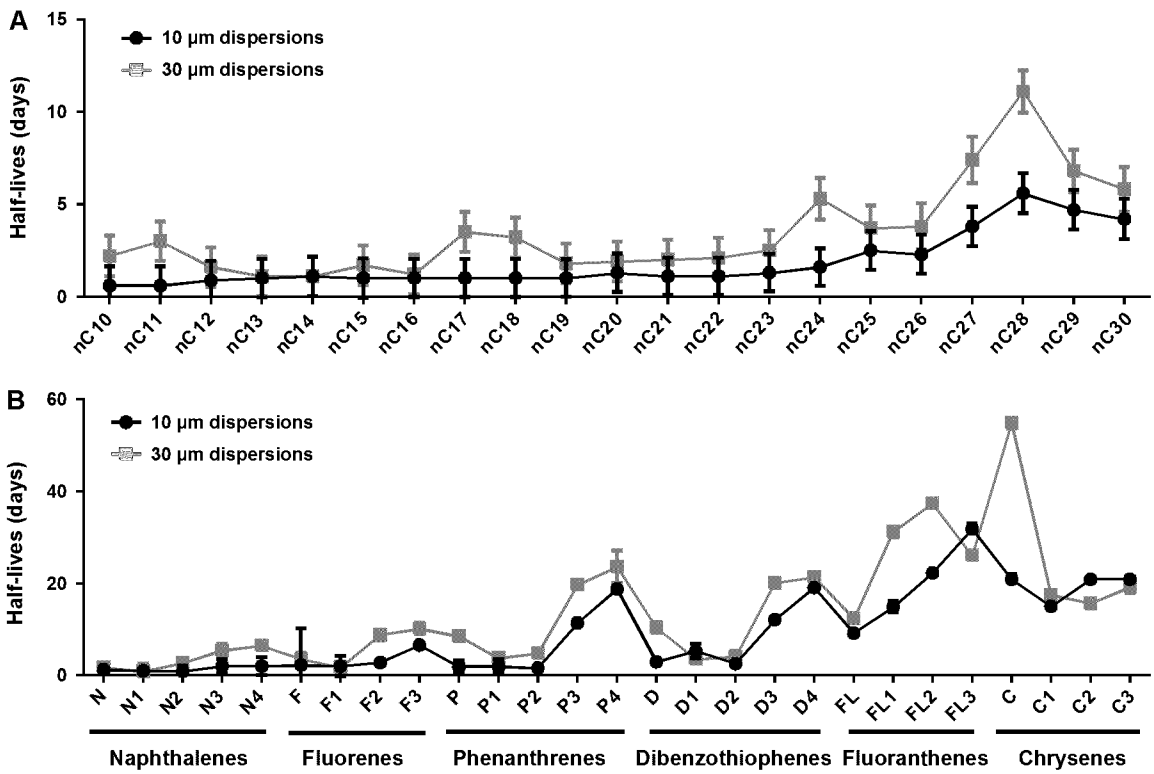


Fig. 4. Half-lives of $nC_{10}$–$nC_{30}$ alkanes (A) and naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, fluoranthenes and chrysenes (B) in 10 l m and 30 l m dispersions with standard deviation errors bars of 3 replicates. Half-lives were determined from rate coefficients without lag-periods included. The numbering of the aromatic groups describes the degree of alkyl-substitution.

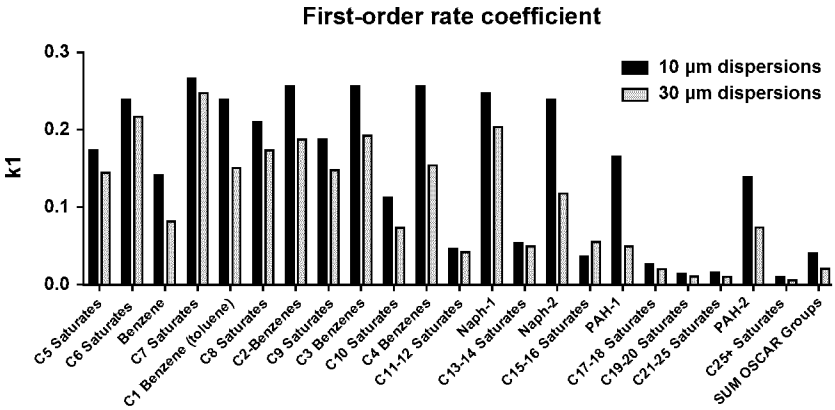


Fig. 5. First-order rate coefficients for oil compound groups of the Macondo oil in 10 and 30 l m dispersions.

transformation had started after 39 days of incubation (Wang et al., 2014), consistent with PAH results from our study.

Oil compound glass wall attachment is well known, and comparison of oil concentrations (TEOC analyses) in water and on glass walls rinsed with solvent (days 0, 8 and 32) showed a gradual increase of wall-attached material, from <3% of total TEOC (day 0), to up to 45% (30 l m dispersions at day 32). Targeted analyses of compounds normalized against 30ab Hopane showed relative preference of 2-ring and non-alkylated 3-ring PAH for the water-phase, while larger alkylated 3-ring and 4- to 5-ring PAH, decalines and n-alkenes gradually distributed between the water- and glass-phase (results not shown). These data emphasize that degradation of dispersed oil in laboratory systems is a result of processes in both water and glass wall surfaces.

### 3.2.3. Biodegradation of oil compound groups

The well-known targeted compounds described above only cover a fraction of the oil. Comparison of TEOC concentrations (GC-FID analyses) with the targeted SVOC and VOC saturate and aromatic oil compound (GC–MS analyses) showed that the sum of the targeted compounds (n-alkenes, 2–5 ring PAH, volatile $C_5$–$C_9$ saturates and $C_0$–$C_5$ benzenes) constituted 33.5% and 40.4% of the sum of TEOC and VOC concentration at the start of the experiment in the 10 l m and 30 l m dispersions, respectively (Supplementary Information, Fig. S6). The TEOC concentrations determined by GC-FID analyses represented 72% and 81% of the oil droplet concentrations measured by the Coulter Counter analyses for the two dispersions, and these results corresponded well with the assumption from true boiling point curves, assuming that $C_5$–$C_{36}$ saturates (boiling points of 27 to approximately 500 fC) represent 70–80% of typical crude oil (Pasquini and Bueno, 2007).

Biotransformation rate coefficients and half-lives of 22 volatile and semivolatile oil compound groups, representing the boiling point range described above (Table S1) were calculated, including $C_5$–$C_{36}$ saturates and 1- to 5-ring aromatic compounds (Reed et al., 2000). The results of Fig. 5 and Table S3 showed rate coefficients of 0.0096–0.2665 (median 0.1692) in the 10 l m dispersions and 0.0054–0.2475 (median 0.0995) in the 30 l m dispersions. These rates resulted in half-lives of 2.8 to 72.2 days (median 4.1 days) and 2.8 to 128.3 days (median 7.2 days) in the 10 and

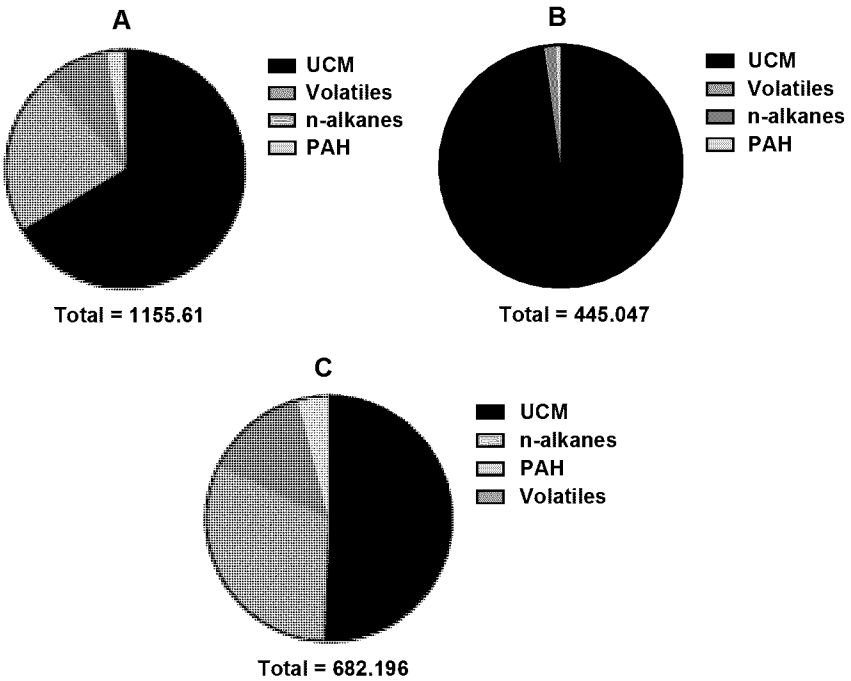


Fig. 6. Distributions of targeted oil compounds and UCM at the start of the biodegradation (A) and after 32 days of incubation in unfiltered (B) and sterilized (C) dispersions. The total concentrations of TEOC (l g/L) are shown below each pie chart.

30 l m dispersions, respectively. The rate coefficients were higher in the 10 l m than the 30 l m dispersions for all oil compounds, except for $C_{15}$–$C_{16}$ saturates. Comparison of the rate coefficients in the two dispersions showed significant differences ($P < 0.05$; Wilcoxon non-parametric t-test). The rate coefficients were higher in favor of the 10 l m dispersions by factors of 1.21 and 1.67 (median values) for the saturate and aromatic compound groups, respectively. The rate coefficients were generally higher for the aromatic (average of 0.175039) than the saturate (0.099304) oil compound groups when data from both dispersions were compiled. This is probably associated with the water-solubility of the aromatic hydrocarbons, as well as the presence of poorly biodegradable branched and cyclic alkanes in the semivolatile saturate groups.

In previous studies we have compared dissolution and biodegradation of oil compounds from thin oil films (10–20 l m thickness) immobilized on hydrophobic adsorbents, showing that fast dissolution of naphthalenes and non-alkylated 3-ring PAH resulted in biodegradation mainly of dissolved compounds, while negligible dissolution of n-alkanes ($nC_{12}$–$nC_{36}$) resulted in biodegradation of these compounds exclusively on the oil–water interphases. For the larger PAH-compounds dissolution decreased with increasing numbers of aromatic rings and alkyl substitution, with biodegradation of these both as dissolved and as oil-associated compounds (Brakstad et al., 2004; Brakstad and Bonaunet, 2006). Oil compound biodegradation is therefore a complex process, involving bacterial communities in the water-phases as well as bacteria attaching the oil surfaces.

The rate for the sum of the 22 oil compound groups in this study was also faster in the 10 l m ($k1 = 0.03984$) than the 30 l m ($k1 = 0.02004$) dispersions, resulting in half-lives of 17.4 and 34.6 days in the two dispersions (Fig. 5; Table S3). Since the sum of these groups may represent most of the oil, these numbers may be used as biotransformation rates for the oil. The oil droplet size was therefore important both for the biotransformation rates of the oil compound groups and the sum of these groups used in this study and presenting a boiling point range of 27–>500 f°C.

The saturates representing the $C_{10}$ to $C_{25+}$ oil compound groups are mostly unidentifiable oil compounds, often termed as the unresolved complex mixture (UCM) (Gough and Rowland, 1990; Killops and Al-Juboori, 1990), and accounts for 60–70% of the groups. Comparison of the sum of TEOC and VOC concentrations with targeted compound groups of n-alkanes, PAH and volatile hydrocarbons showed that the UCM became the predominant oil fraction during the biodegradation period (Fig. 6; Fig. S6, Supplementary Information). Several studies have shown that the UCM fraction includes compounds that are not readily susceptible to biodegradation (Reddy et al., 2002; Booth et al., 2007). The UCM was predominant in each of the saturate groups from $C_{11}$–$C_{12}$ to $C_{25+}$ (Table S1). The degradation of these compounds decreased by increasing boiling point ranges in both 10 l m and 30 l m dispersions (Table S3), and the rate calculations showed that their degradation was mainly faster in the 10 l m than the 30 l m dispersions (Fig. 5; Table S3).

The result from the current study show that reduced oil droplet sizes resulted in increased biodegradation rates. The use of chemical dispersants will generate small droplet oil dispersions, and the result from this and other studies (e.g. Siron et al., 1995; Venosa and Holder, 2007.; Prince et al., 2013; McFarlin et al., 2014; Brakstad et al., 2014) demonstrate that the use of dispersants to generate small droplets will promote biodegradation in seawater at different environmental conditions. Dispersants like Corexit 9500 are considered to have moderate to low acute toxicity (e.g. Mitchell and Holdway, 2000; Judson et al., 2010), and surfactants like alkyl sulfosuccinates may be biodegradable (Garcia et al., 2009; Bælum et al., 2012). The positive influence of chemical dispersants on the biodegradation of potentially toxic oil compounds may therefore compensate for possible negative effects of dispersant components in the marine environment.

Operationally, dispersants have mainly been used for surface oil spills to remove the slick from the seawater surface by generation of small droplet dispersions in the water column. We have previously shown that oil compounds in surface oil emulsions are poorly biodegradable compared to chemically dispersed oil (Brakstad et al., 2014). The dispersant application during the DWH incident aimed at reducing surface slick generation and may also have contributed to the generation of the small oil droplets in the Macondo deepwater plume. If deepwater injection of dispersant during an oil spill is able to reduce oil droplet size and avoid oil surfacing, this may enhance oil compound biodegradation and thereby additionally reduce the impacts of the spill. However, it is important to emphasize the lack of knowledge related to the many unidentifiable oil compounds, both with respect to biodegradability and toxic effects.

Although the water used in the current study was Norwegian coastal seawater, the results may be related to the Macondo deepwater plume. Both oil, oil droplet size distribution (North et al., 2011) and seawater temperature was similar in the current experiment and the DWH deepwater plume. Our experiments were performed at atmospheric pressure, but laboratory experimental studies have shown that bacteria associated with deepwater plume biodegradation of the Macondo oil also biodegraded the oil at atmospheric pressure (Hazen et al., 2010; Bælum et al., 2012).

## 4. Conclusions

The study presented here compares, for the first time to our knowledge, biodegradation rates in oil dispersions with pre-defined droplet sizes, and under temperatures relevant for a deepwater discharge. The results of this study showed that biodegradation of alkane and aromatic hydrocarbons in a dispersible oil (Macondo) was faster in 10 l m than 30 l m dispersions for targeted oil compounds and oil compound groups, as well as the sum of the groups representing most of the oil. These data indicate that dispersant treatment of deepwater oil spills will be beneficial for the oil compound biodegradation, if oil droplet sizes are reduced. Our data showed good agreement with results from other biodegradation studies performed with chemically dispersed oil at low seawater temperatures. Although the current study was performed in seawater from a Norwegian fjord and under atmospheric pressure, these data may also have relevance for the DWH deepwater oil plume. We used the same oil, similar temperatures (4–5 f°C), and oil droplet size distributions were comparable to the DWH deepwater plume. Published oil compound degradation data with GoM seawater or enrichment cultures also showed agreement with our results. Comparison of fate model predictions, laboratory results and field data may further substantiate the fate of oil dispersions in deepwater spills and improve the information concerning the impacted deepwater area of a spill. This information is important to include in risk assessment analyses.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.marpolbul.2015.02.006.

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**14th Annual OSC Readiness Training Program**

# 2011 OSC Readiness Training

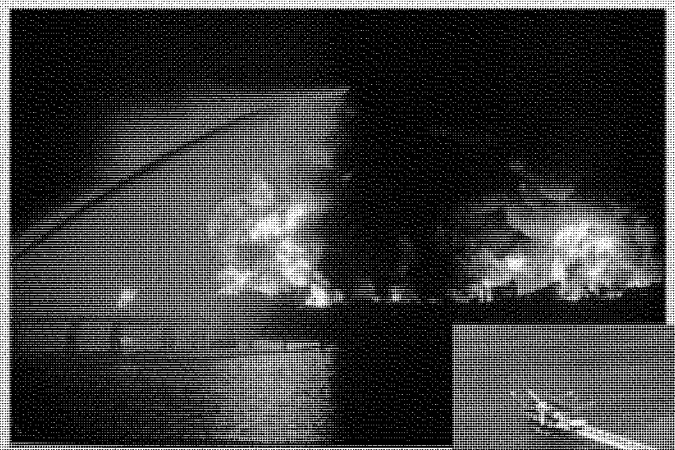
NCP Product Schedule / Selection Guide for Oil Spill Response Technologies / Alternative Response Tool Evaluation System for Oil Spill Response (ARTES)

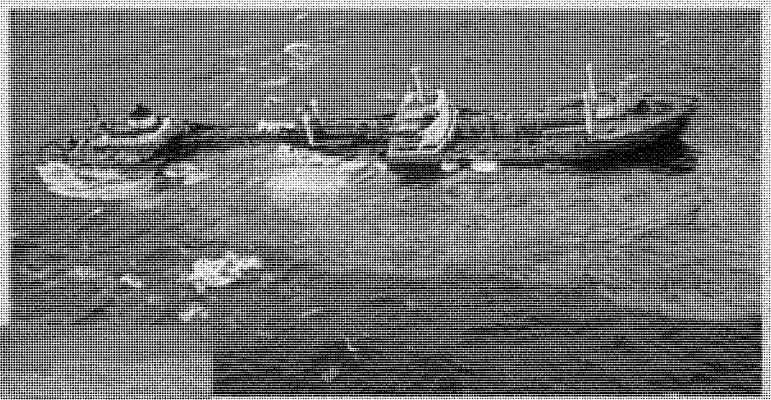
Training by OSCs for OSCs

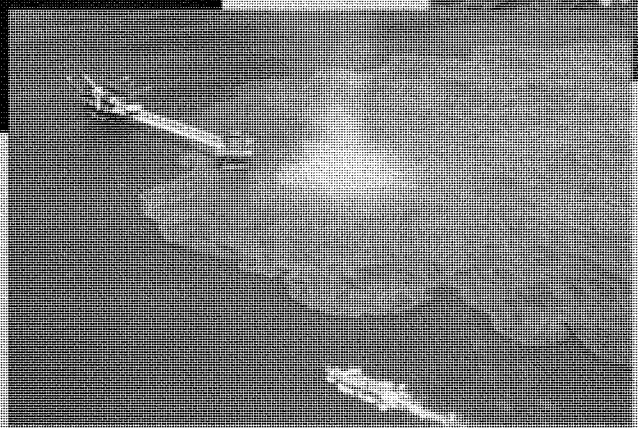
**January 31 – February 4, 2011**
**Orlando, Florida**
**www.oscreadiness.org**

# History and Background

- Past spill experiences shapes our current decision-making about countermeasures e.g., *Torrey Canyon*, *Ixtoc I* blowout, *Exxon Valdez, etc.*











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# History, Cont.d

- Use of "non-traditional" response technologies (e.g., early dispersants) ⇒ perceived damages
- Their use resulted in changes in Federal regulations:
  - National Contingency Plan, and
  - the Oil Pollution Act of 1990





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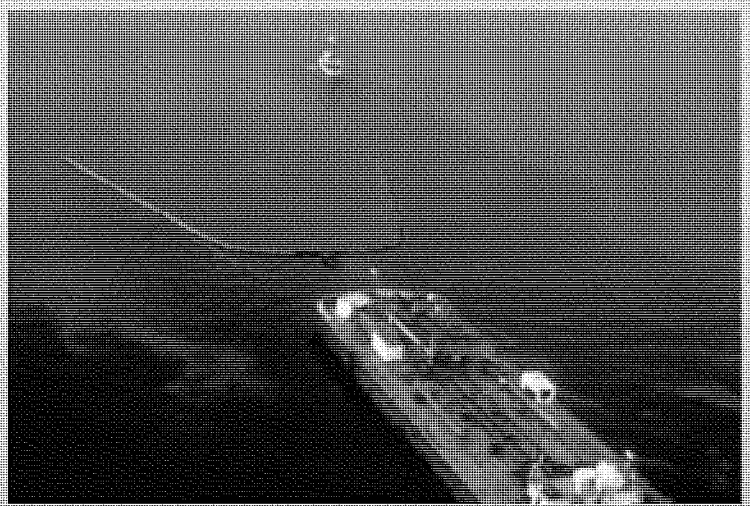
# High Comfort Level

- Traditional countermeasures (boom, skimmer, sorbents etc.) are a known entity



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# Oil Spill Technologies, Defined

- a.k.a. – "non-traditional" regulated countermeasures
- Countermeasures that are infrequently used; limited experience / knowledge about when these countermeasures could be useful and environmentally beneficial





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# Oil Spill Technologies, Defined

- Includes:
  - Dispersants
  - Bioremediation Agents
  - Surface Washing Agents
  - Shoreline Pre-treatment Agents
  - Surface Collecting Agents
  - Solidifiers
  - Elasticity Modifiers
  - Emulsion Treating Agents
  - Other Miscellaneous Agents





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# Discomfort with Oil Spill Technologies

- Decision-maker's wary of non-traditional response technologies

# Why?

- Lack of experience with the various products / strategies
- Perceived problems with their use:
  - Regulatory agency understanding?
  - Liability?
  - Result in additional environmental damage?
  - Lack of experienced application / recovery personnel
  - Difficult to interpret product information?
  - Vendors





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# Technologies Today

- Chemical products significantly changed fro past formulations; research now current and extensive on many products
- Standardized effectiveness and toxicity testing required
- Must be registered with EPA for use on oil spills in the US





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# Approach For Evaluating Technologies

- "Tools" available to response decision-makers:
  - The National Contingency Plan (NCP) Product Schedule (Subpart J - 40 CFR Part 300.900)
  - Selection Guide for Oil Spill Response Technologies
  - Applied Response Tool Evaluation System (ARTES)





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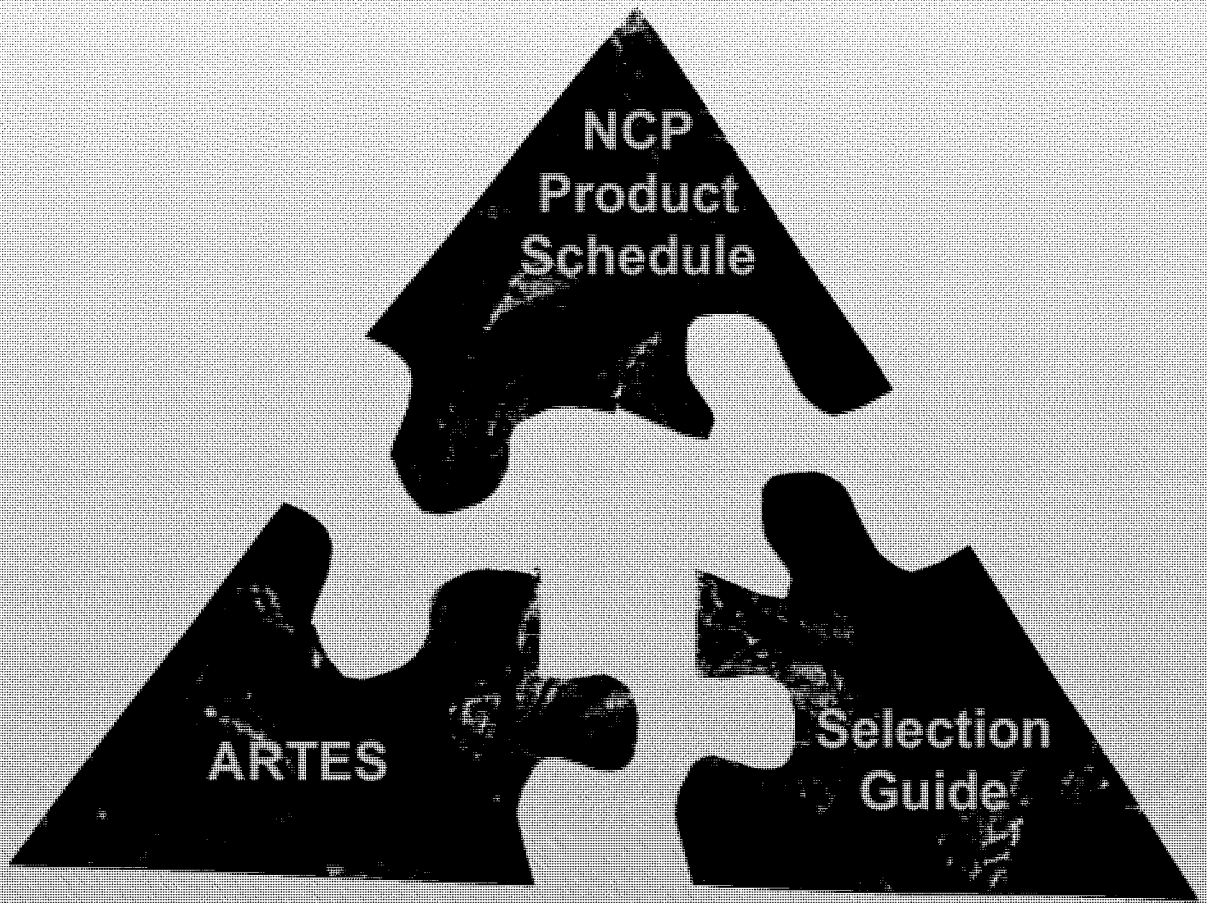
# Putting the Pieces Together for Response Decision-making

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# NCP Product Schedule

- Functions as the regulatory vehicle for use of any applied technologies
- Regulated under:
  - Section 311(d)(2) of the Clean Water Act, and
  - Section 4201 (a) of the Oil Pollution Act of 1990



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**Listing of a product does NOT mean that the product is recommended or endorsed by the USEPA for use on an oil spill;**

**Only that product has met minimum information requirements for listing.**





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# Product Categories on NCP PS

- Dispersants
- Surface Washing Agents
- Surface Collecting Agents
- Bioremediation Agents
- Miscellaneous Oil Spill Control Agents





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# Limitations of NCP PS

- Not designed for incident-specific decision-making
- Does not allow easy comparison of products
- No way to capture lessons learned for individual product use
- Limited to chemical and biological additive products, that is…not new or advanced mechanical strategies or techniques



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# Alternative Response Tool Evaluation System (ARTES)

- Focus of another presentation…
- Used to:
  - evaluate a product's appropriateness for use during a specific incident, under specific circumstances.
  - as a pre-evaluation to identify conditions under which favorable outcomes are anticipated when a product is used.





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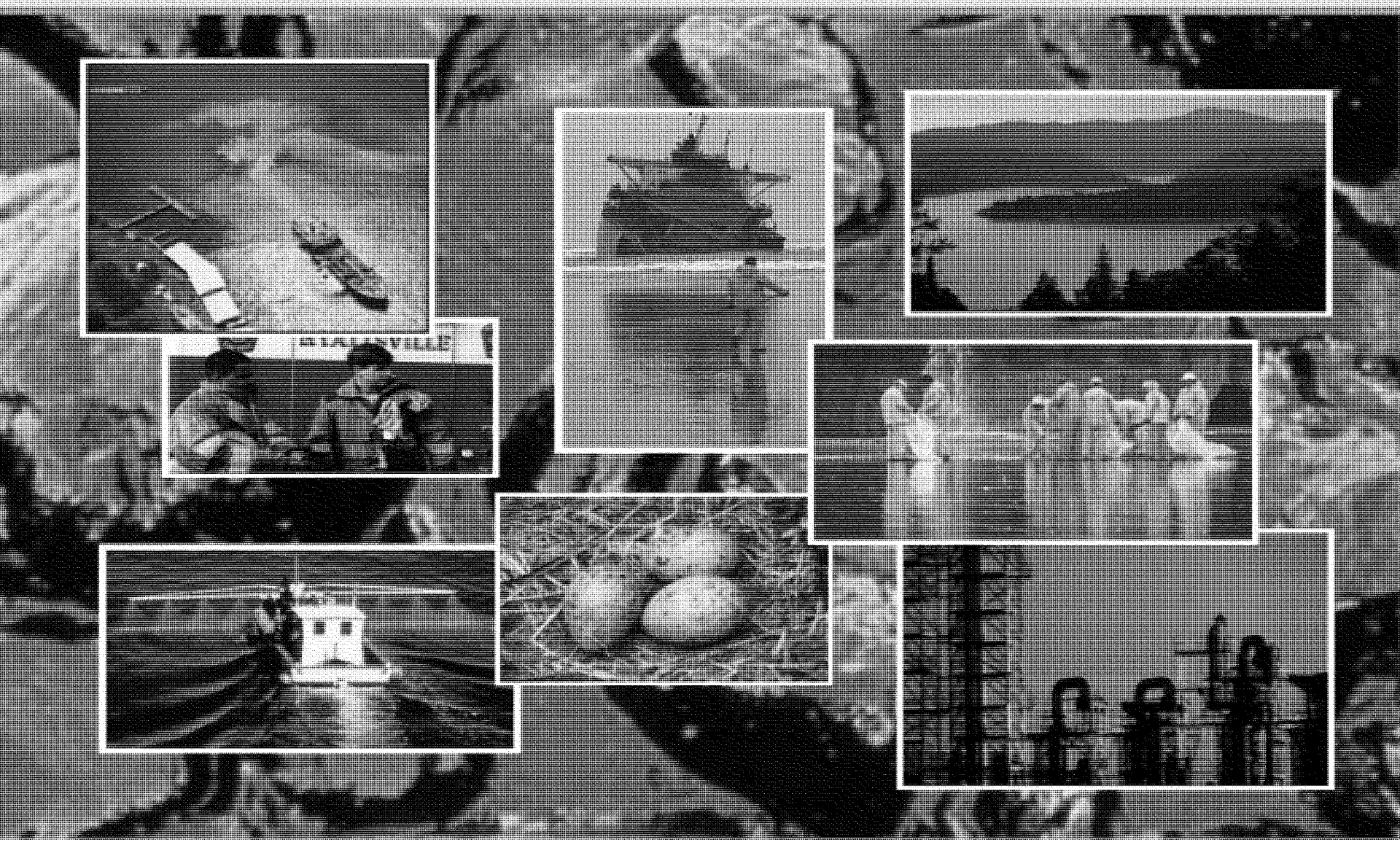
# Selection Guide for Oil Spill Response Countermeasures



# Why Selection Guide Developed

- Designed to provide OSCs and other response decision-makers with an easy-to-use technical guidance database for considering applied oil spill technologies for use during an incident.
- Developed by Region III in cooperation with Region IV





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# Selection Guide, Cont'd

- Two volumes:
  - Decision-making information (Nationally applicable) and
  - Implementation/operational support documentation (regionally customizable)
- Provides information requested by decision-makers to consider, select, and implement an environmentally-appropriate product or technology





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# Selection Guide Information

- Bioremediation Agents
- Dispersants
- Elasticity Modifiers
- Emulsion Treating Agents
- *In situ* Burning on Land
- *In situ* Burning on Water
- Shoreline Pre-treatment Agents
- Solidifiers
- Sorbents
- Surface Collecting Agents
- Surface Washing Agents

***Different Categories than the NCP!***





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# Information, Cont'd

- Information Categories
  - Mechanism of Action
  - When to Use
  - Authority Required
  - Availability
  - General Application Requirements
  - Health and Safety Concerns
  - Limiting Factors/ Best Management Practices
  - Monitoring Requirements / Suggestions
  - Waste Generation and Disposal Issues
  - References





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# Content

- Instructions and matrices for selecting a strategy or countermeasure using job aid techniques
- Allows direct product comparisons among products and categories/strategies using product comparison tables
- Establishes the need for monitoring and capturing lessons learned





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# Content, Cont'd

- Glossary used with various products/ strategies
- History and status of product use (case study examples)
- Toxicity primer – how toxicity is measured and what the numbers really mean





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# Strengths of Selection Guide

- Allows comparison of similar products as well as comparison of various strategies to determine the best response
- Developed using "job aid" techniques
- Allows documentation for the decision-making process





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# Strengths, Cont'd

- Provides situation–specific assistance in the selection of products and strategies during planning and response, including new products / strategies
- Provides guidance on the use of response technologies and products
- Developed to capture and incorporate lessons learned





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# Limitations of Selection Guide

- Only as good as the information submitted; data could be limited
- Should be updated as new information becomes available (e.g., ARTES evaluations, actual use)
- June 2009 Edition available in:
  - paper format,
  - internet download (January 2003) from www.response.restoration.noaa.gov/oilaids.html
  - interactive e-version (to be released soon)





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# Limitations, Cont'd

- Decision-makers need to ensure that they are making their decisions with the most current information available
- Not a cook book! – Still have to evaluate incident-specific information with product(s) in mind
- Need Evaluation Team (OSC, SSC, State, USFWS, etc.) to assist with review to ensure effective evaluation for incident-specific conditions for FOSC.





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# e-version of the Guide

- e-version of the Selection Guide finalized
  - Components & use focus of training after lunch
  - Hands-on practical use of the guide
    - Example scenarios will be used to work through the Selection Guide Process
    - Input your own scenarios





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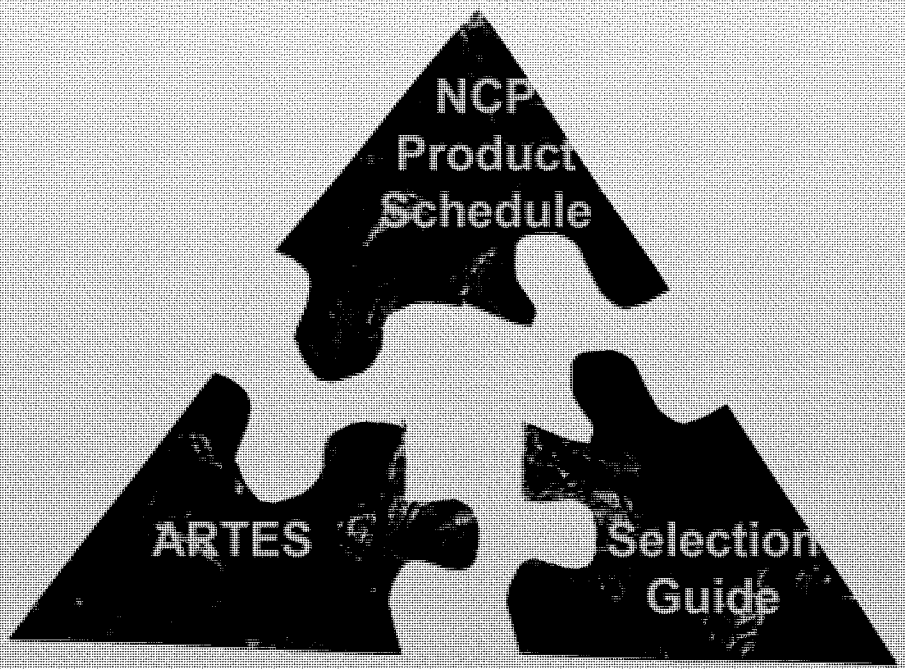
# In Summary

- Use all the pieces to solve the puzzle (make a decision)



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# In Summary, Cont'd

- Most effective use of these tools is in a coordinated manner
- NCP is the first step and requirement; provides guiding legislation; Nationally applicable information
- ARTES assists in the evaluation of single product / technology for regional or incident-specific conditions





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# In Summary, Cont'd

- Selection Guide allows:
  - Screening the incident for possible strategies/ products that could add value to a response, and
  - Comparison of products / strategies of interest relative to other techniques to select the most appropriate technology





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# Thanks for your attention!

If you have any questions, please call
Debbie Scholz
843-367-5126

# 14th Annual OSC Readiness Training Program

# OSC Training-Orlando, FL-2010
# Alternative Countermeasures

Presenter: Albert D. Venosa, Ph.D.
U.S. EPA-ORD
Director, Land Remediation & Pollution Control Div.
National Risk Management Research Laboratory
Cincinnati, OH 45268
Date: February 3, 2010

Training by OSCs for OSCs

January 31 – February 4, 2011
Orlando, Florida
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# Outline of Presentation

- Two technologies to be discussed
  - Bioremediation
    - Definitions
    - Overview
    - The Process
  - Dispersants
    - Factors needed for effectiveness
    - Wave tank studies
  - Spill scenarios





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# BIOREMEDIATION

# What is bioremediation?

- The exploitation of living microorganisms to convert organic contaminants into biomass and innocuous end products
  - Innocuous end products include $CO_2$, water, and incompletely oxidized organics





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# How Biological Clean-up Is Achieved

- Naturally, without human intervention
  - Called "Natural Attenuation (NA)" or "Monitored Natural Attenuation (MNA)"
- Accelerated (requires human intervention)
  - Bioaugmentation
  - Biostimulation





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# Natural Attenuation

- The disappearance of oil via natural means, including:
  - Volatilization
  - Washout
  - Biodegradation
  - Photolysis

# Basics of Biological Treatment





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# Composition of Living Matter

- Among other trace substances, the primary components are:
  - Carbon: basic structural component of protoplasm and biomolecules
  - Nitrogen: used in formation of amino acids for protein synthesis
  - Phosphorus: used in formation of genetic material, high energy bonds, and membranes





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# What are hydrocarbons?

- Organic compounds containing carbon and hydrogen
  - May contain fully saturated bonds (no double bonds) (alkanes)
  - May contain some unsaturated bonds (double bonds) (alkenes)
  - May be linear or cyclic and saturated (cyclohexane, hopane)
  - May be aromatic with single or fused rings (benzene, phenanthrene)
- When oil is spilled into the environment, it becomes food for living microorganisms able to utilize it for growth





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# What is the goal of a microorganism?

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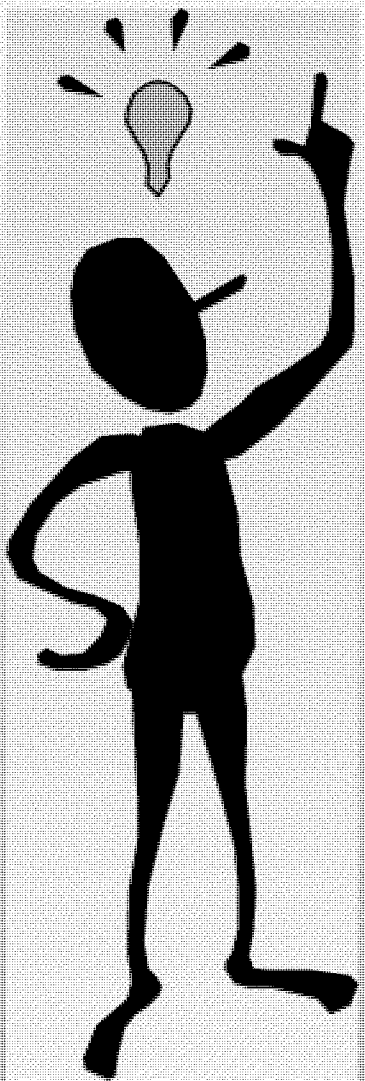
# To make another microorganism!







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# Process of Biodegradation

- Converting food into biomass requires several steps
  - 1st step is addition of OH-group to alkane or PAH ring forming an **alcohol** (R-OH)
  - Progressive **oxidation** to aldehyde (R-CHO), then to acid (R-COOH) leading to chain length reduction
  - As oxygen added to hydrocarbons, compounds become more polar, more water soluble
  - Polar compounds less toxic, more biodegradable
  - In case of PAH, **ring fission** occurs followed by chain length reduction as above
- Eventually to water, $CO_2$, biomass, and innocuous end products





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# Biodegradable Components of Petroleum Oils

- Alkanes (saturates): easy
- Polycyclic Aromatic Hydrocarbons (PAHs): moderate
  - Fused aromatic rings, must be split
  - Biodegradability depends on number of rings and alkyl substituted groups
- Heavy polar compounds (NSO): difficult
- Asphaltenes: very difficult, complex

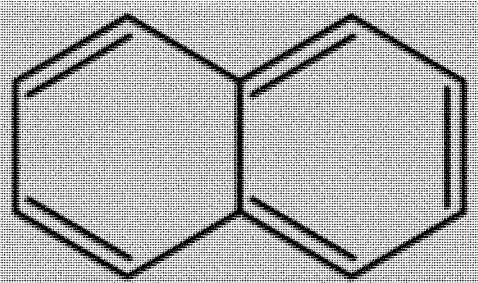
# Examples

- Straight Chain Alkanes: easy to degrade. Example: HEPTADECANE (17 carbons)

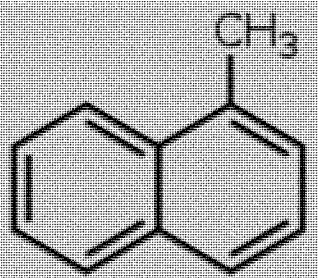
- Branched alkanes: harder to degrade. Example: PRISTANE (19 carbons)

- PAHs

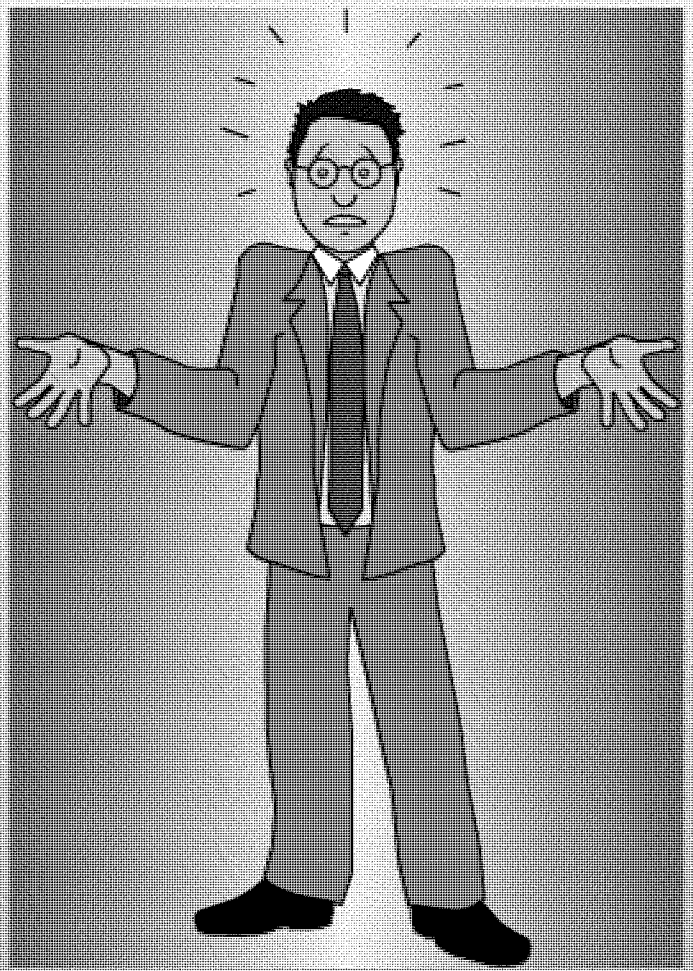
(parent, easier)



(alkyl-substituted, harder)



# What are the requirements for successful bioremediation?







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# Requirements for Success

- Bacteria with metabolic capabilities must be present
- Rates of growth can be maximized by ensuring that:
  - Adequate supplies of oxygen and nutrients must be present
  - pH between 6 and 9
  - No other adverse circumstances
    - High salt content
    - Low moisture
- Weight of oil affects success (lighter oils more biodegradable, asphaltenes tend to inhibit diffusion)
- Oil surface area important because biodegradation occurs at oil-water or oil-sediment interface





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# Where are oil degraders found?

- Hydrocarbons are found everywhere
- Hydrocarbon degraders are found everywhere





ED_001324_00007288-00017

# An oil spill causes huge influx of carbon (food). How does an organism cope?

- To convert carbon to biomass, bacteria must have nitrogen and phosphorus and oxygen
- Bacteria will grow slowly in presence of usual amounts of N and P in nature
- To maximize rate, give more N and P
- May need to provide oxygen





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# Bioremediation Approaches

- Bioaugmentation
  - The addition of highly competent microbial cultures to an impacted site to accelerate or kick-start the biodegradation process.
- Biostimulation
  - The addition of factors (usually nutrients) that limit the ability of the degrading populations to grow at their maximum rate.





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# Assumptions for Successful Bioaugmentation

- Culture must be able to grow rapidly on oil
  - Can be determined in lab (NCP product testing)
- Culture must be able to colonize the environment rapidly and out-compete the natural communities
  - Very difficult to accomplish





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# Quiz Question:

Based on what you know so far, do you think adding a living culture to a spill site will accomplish the cleanup goal?

Why or why not?





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# Answer

- No need to add cultures to an oil spill
- Bacteria need what is lacking: N and P, and if the environment is anaerobic, also need oxygen
- We have 2 guidance documents that describe how to calculate and add nutrients to an oil spill site
  - Available on EPA website:

http://www.epa.gov/emergencies/publications.htm#bio





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# Wetland Environments

- Oil spills very likely to affect coastal marshes and wetlands
- Most research data available are ORD-funded studies in Quebec and Nova Scotia





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# Properties of Wetland Environments

- Usually oxygen limited, very quiescent (little wave action)
  - Become anaerobic a few mm below ground surface
- Likely not nutrient-limited
  - However, plants easily out-compete bacteria for available nutrients





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# How is bioremediation applied to wetlands?

- Depends on goal:
  - If oil removal is main goal, natural attenuation may be the favored strategy, especially if penetration took place
    - Biostimulation might still be appropriate if significant penetration has not occurred
  - If ecosystem recovery is main goal, nutrient addition may speed restoration substantially





ED_001324_00007288-00025

# Plot Recovery in St. Lawrence River Study, Mid-Summer

ED_001324_00007288-00026

# Plot Recovery, St. Lawrence River, end of summer

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# Plot Recovery, St. Lawrence River, 2nd year

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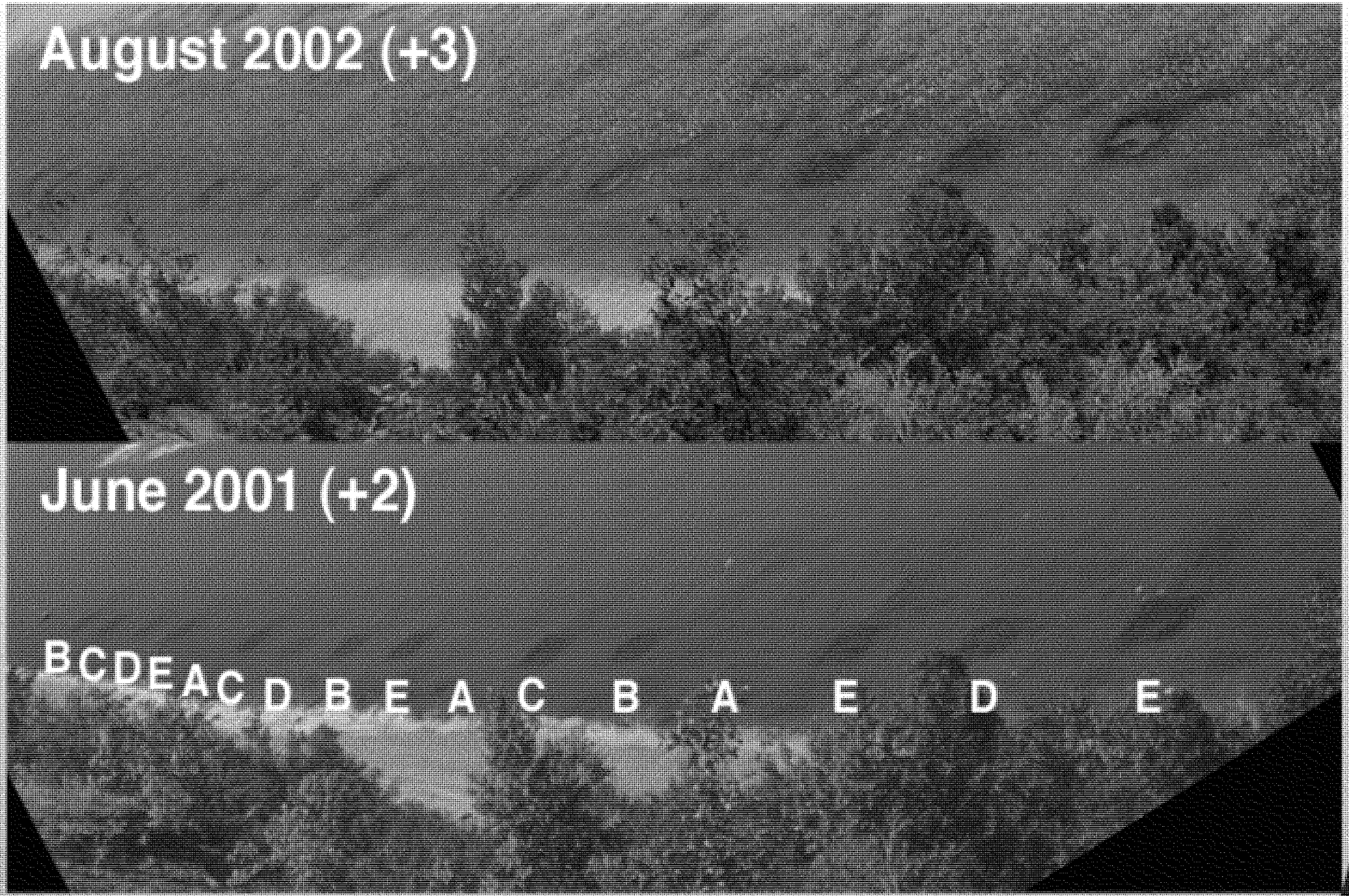




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# Land Bioremediation

# Properties of Terrestrial Environments

- Lateral spread of oil less widespread than in coastal wetlands or beaches
- Ecological damage typically localized and limited
- Problem: vertical movement to water table





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# Land Farming

- Same principles apply:
  - Maintenance of supply of nutrients
  - Maintain aerobic conditions
    - At shallow depths, tilling
    - At deeper depths, bioventing or excavation followed by *ex-situ* techniques like biopiles or composting
  - Fertilizer needs for land treatment
    - Typically, ratio of 100C:10N:1P used (minimize use of nitrate)
    - Prefer adding in several increments, not all at once





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# Factors Affecting Land Treatment

- pH control neutral to slightly alkaline (6.5 to 8.5)
- Moisture important
- Nutrients
  - Without spill, microbial activity usually limited by carbon
  - After spill, N and P usually limiting





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# Vegetable Oil

- Properties similar to petroleum
  - Light nonaqueous-phase liquid (LNAPL)
- Coating of feathers, fur, and gills is harmful
  - Absence of odor and sheen results in reduced avoidance
  - Reduces thermal insulation and buoyancy
- May burn if ignited
- May clog water treatment plants (due to the polymerization property)
- Surface oil may prevent re-aeration of water column





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# Composition of Vegetable Oils

- Triglycerides
  - Long chain fatty acids coupled to glycerol, a 3-carbon compound with 3 alcohol (-OH) groups
  - Fatty acids are long chain alkanes (saturated) or alkenes (unsaturated) with a carboxylic acid group at end (-COOH)
    - To make a triglyceride, the fatty acids replace the –OH groups
  - Examples
    - Stearic acid (18 carbons with no double bonds)
    - Oleic acid (18 carbons with one double bond)
    - Linoleic acid (18 carbons with two double bonds)
    - Linolenic acid (18 carbons with three double bonds)





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# Chemical Effects of Vegetable Oil Spills

- High BOD may cause oxygen depletion
  - Greater effect on DO than petroleum oils
- Unsaturated oils (liquids at cold temperatures) are subject to chemical (abiotic) oxidation
  - Polymerization due to chemical oxidation and cross-linking
  - Rancid odors may develop rapidly
  - Unsaturated oils form gum balls and varnishes
- Saturated oils turn solid at cool temperatures
- May be toxic or form toxic products
  - Especially free fatty acids and chemical oxidation products





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# Biodegradability of Vegetable Oils

- Degradable both aerobically and anaerobically
  - Because they're already oxygenated (fatty acids), anaerobic biodegradation can proceed rapidly
  - This distinguishes these oils from petroleum oils
- If polymerization occurs, biodegradation is inhibited
  - Gumball and varnish formation





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# DISPERSANTS

# What are dispersants?

- Compounds that contain one or more surface active agents (surfactants) and possibly a solvent
  - Surfactants reduce the oil-water interfacial tension
  - Solvents reduce oil viscosity
- When applied to a slick, small droplets are formed that intermix in the water column, increasing the surface area of the oil





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# What makes dispersants effective?

- Properties of the oil
  - Viscosity
  - Weight
- Slick thickness
- Dispersant:oil ratio (DOR), best at 1:25 to 1:50
- Surfactant loss at the water surface
- Surface tension of water
- Salinity
- Mixing energy due to wave action





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# Importance of Mixing Energy

- Dispersion takes place at small scale (< 1 cm)
  - Simulation in lab possible since small eddies similar to eddies at sea
  - Energy dissipation rate per unit mass is the measure of mixing energy
    - Units are Watts/kg water
    - Dissipation of kinetic energy due to laminar and turbulent shears, which are directly proportional to velocity gradients
    - Measure velocity gradients to compute energy dissipation rate





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# Wave Tank at Halifax, NS

- A collaboration between EPA and Fisheries & Oceans Canada (DFO)
- Wave tank fabricated at the Bedford Institute of Oceanography (BIO), Dartmouth, NS
- Objective: to study dispersant effectiveness at various mixing energies representative of sea states
  - Experiments have taken place to define energy of breaking and non-breaking waves
  - Batch and flow-through conditions





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# Characteristics of Wave Tank

- Dimensions: 32 m x 2 m x 0.6 m
- Materials of construction: epoxy-coated steel
- Computer-controlled wave maker able to produce regular and breaking waves
- Wave absorbers to mitigate reflection
- Can be drained and filled in < 2 h
  - Allows for cleaning between runs to prevent residuals from confounding experiments
- Can be operated in batch and flow-through modes





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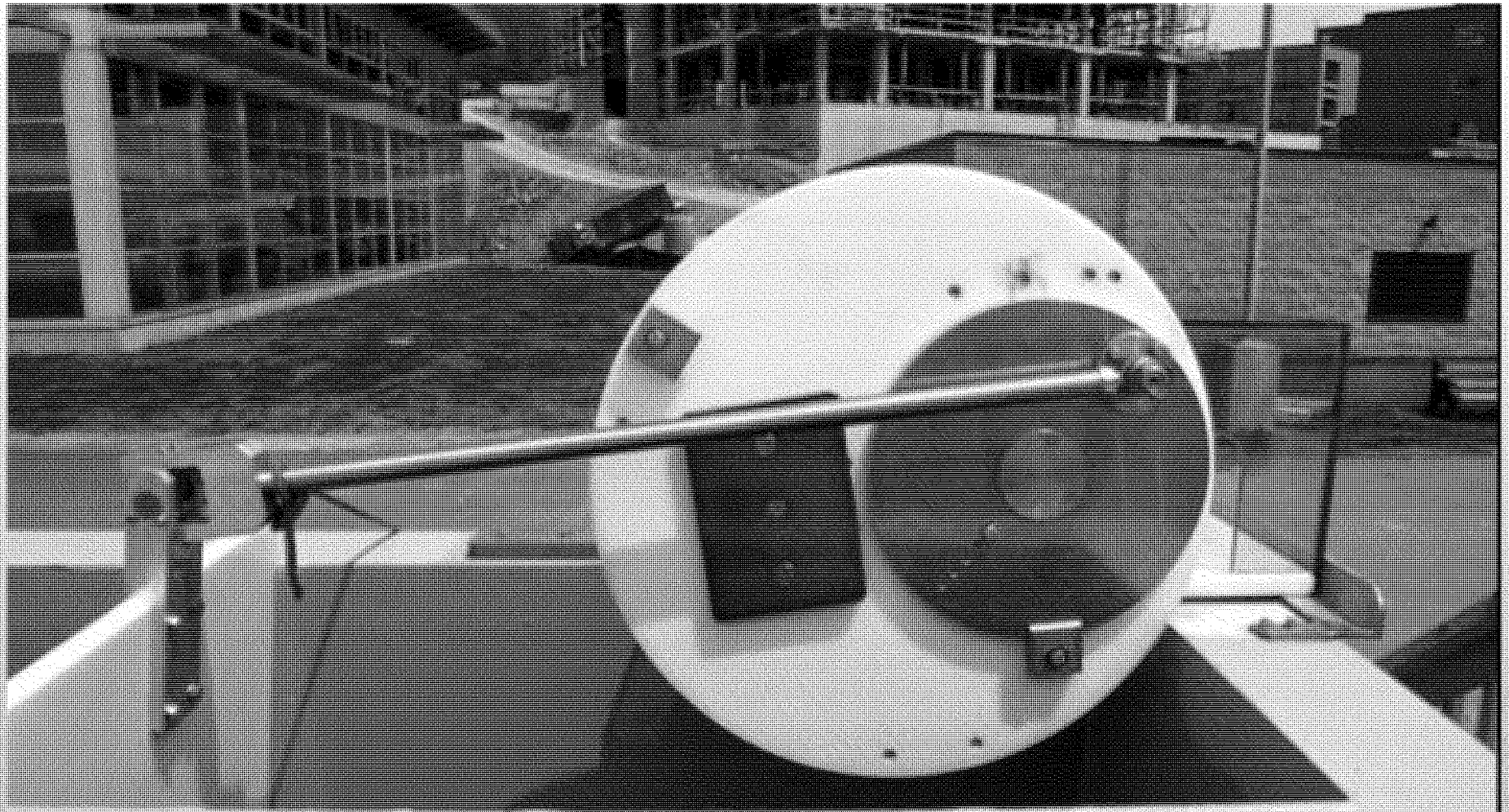
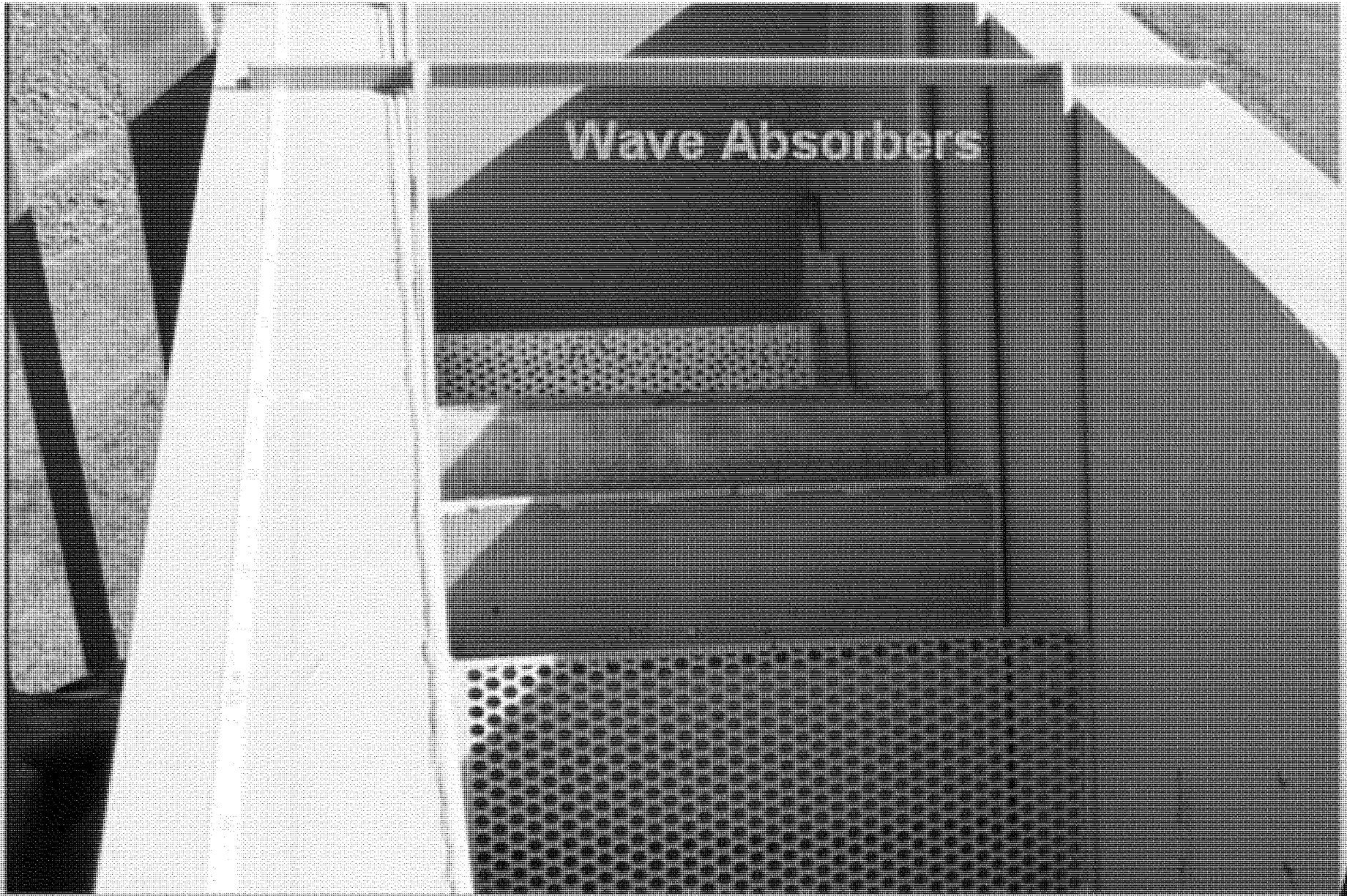


Wave Maker



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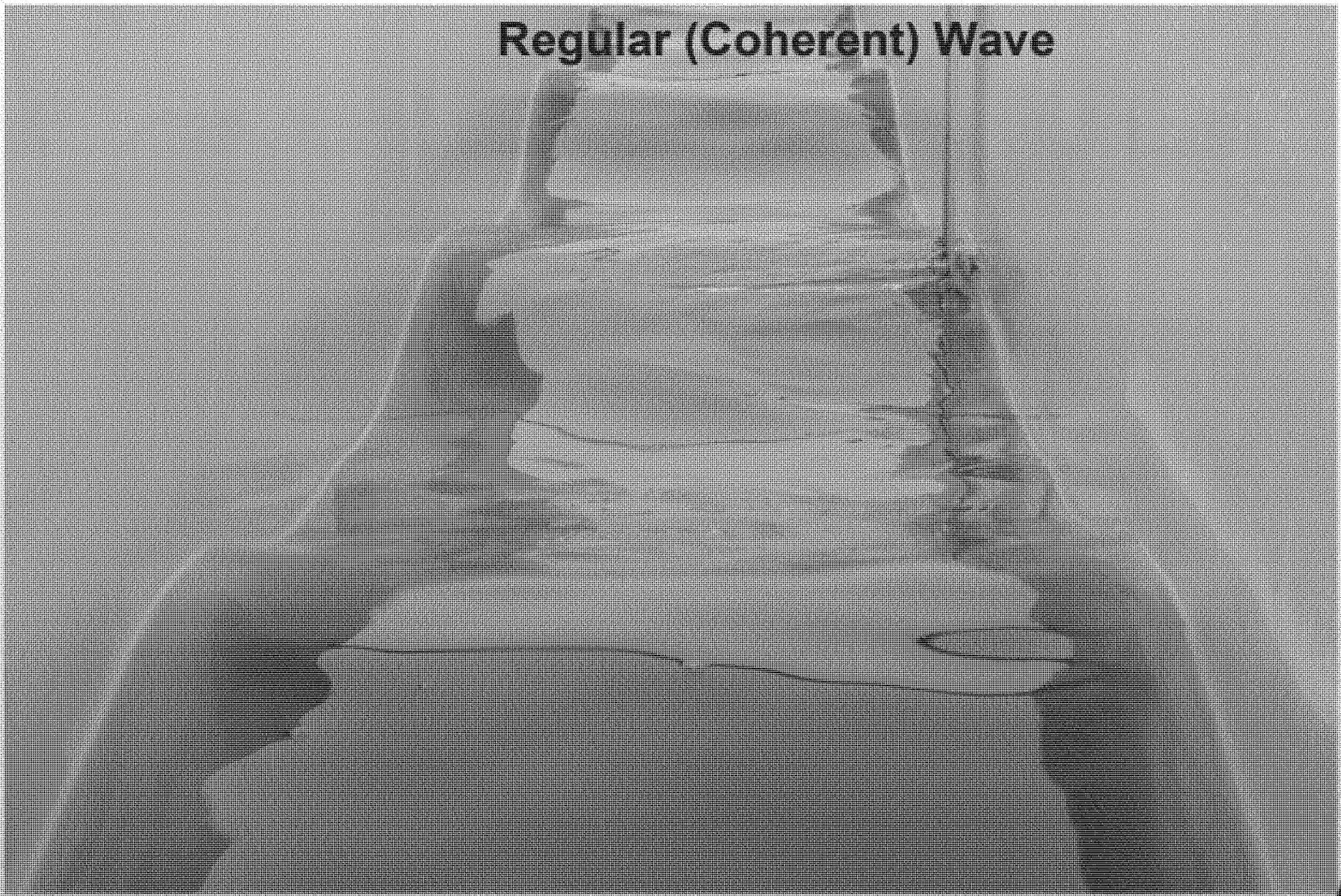
# Regular (Coherent) Wave





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# Mild, Spilling Breaker

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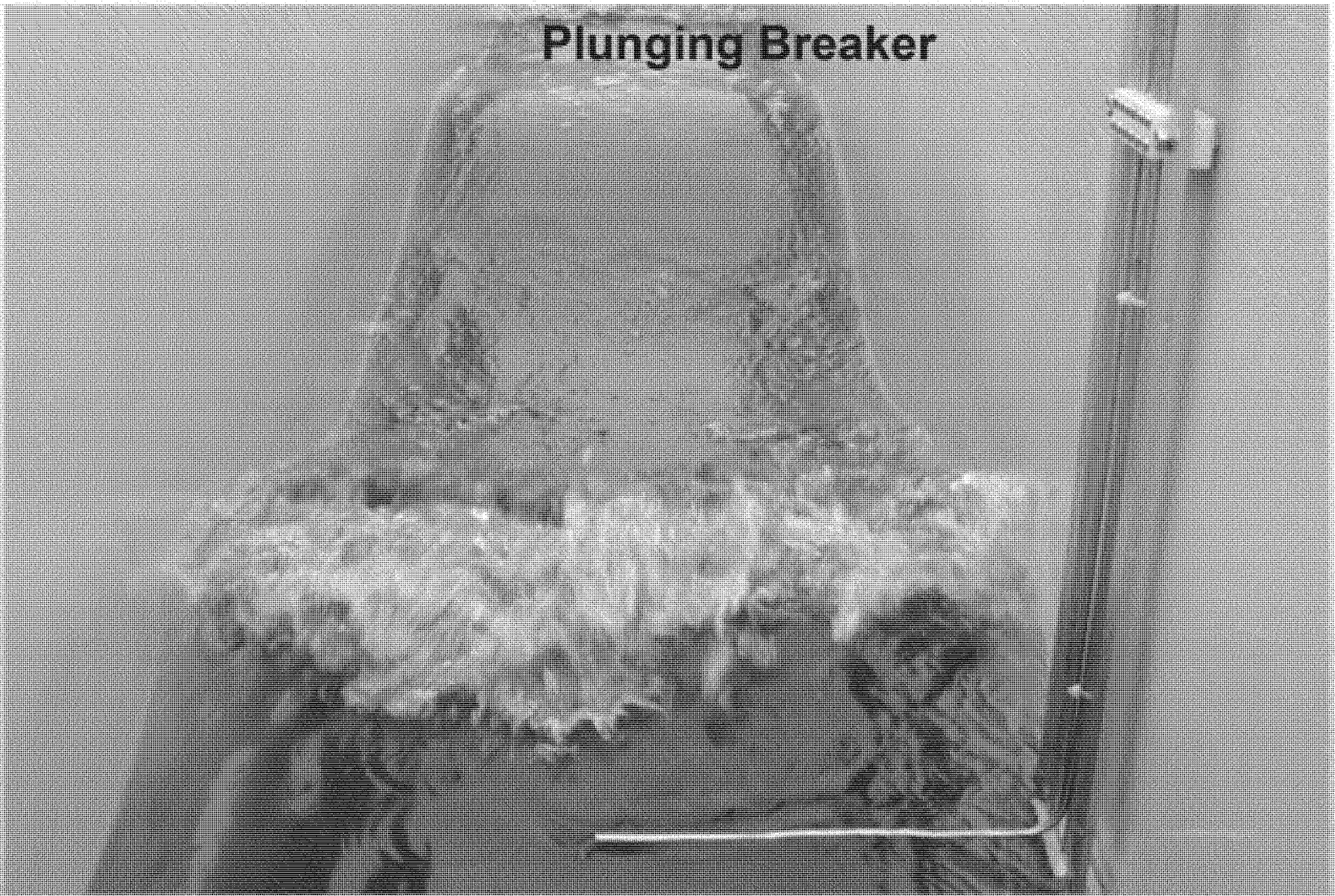
Plunging Breaker

# Dispersant Effectiveness

- Breaking waves are important for effective and lasting dispersion
  - Breaking waves shear oil slick into tiny droplets that don't easily recoalesce
  - Breakers push oil downwards into water column where currents may carry the dispersed oil away
- Regular waves disperse oil somewhat but do not impart sufficient energy to break up the oil into small droplets or push the droplets down deeply into the water column
  - They do maintain sufficient energy to maintain dispersed state
- Mineral fines enhance dispersion of oil into water column





ED_001324_00007288-00049

# Summary of Dispersant Use in Gulf Spill

- EPA science team developed sampling and monitoring plan for deep sea injection and surface application
- Called for measurement of:
  - Dispersed oil by fluorometric techniques
    - CDOM (colored dissolved organic matter)
    - CTD (conductivity, temperature, depth)
    - More advanced but proven techniques (fixed wavelength)
  - Droplet size distribution (LISST)
  - Analytical chemistry (GC/MS and TPH) of batch samples
  - Dissolved oxygen
    - Hypoxic level was 2 mg/L (or 1.4 mL/L)
  - Toxicity by rotifer assay (Rototox)





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# Subsurface Injection of Dispersant

- **Volume based on DOR, high degree of uncertainty**
  - Optimum volumetric DOR ~ 1:25 to 1:50
  - Flow rate of oil unknown for first 30 days
    - Originally thought to be 5,000 bbl/d (210,000 gpd)—gave a DOR of 1:14 (too much dispersant)
    - Later adjusted higher and higher to final flow of 62,000 bbl/d (2.6 million gpd or a DOR of 1:174 (too little dispersant)
    - Due to uncertainty of ecological effects, dispersant use was fixed at 15,000 gpd for spill duration
- **Dispersed oil plume detected consistently at 1,100-1,300 m**
  - Moving predominantly in SW and NE directions (isobath flow)
  - Active natural seeps mapped at 12 SW and 17 km NE of wellhead





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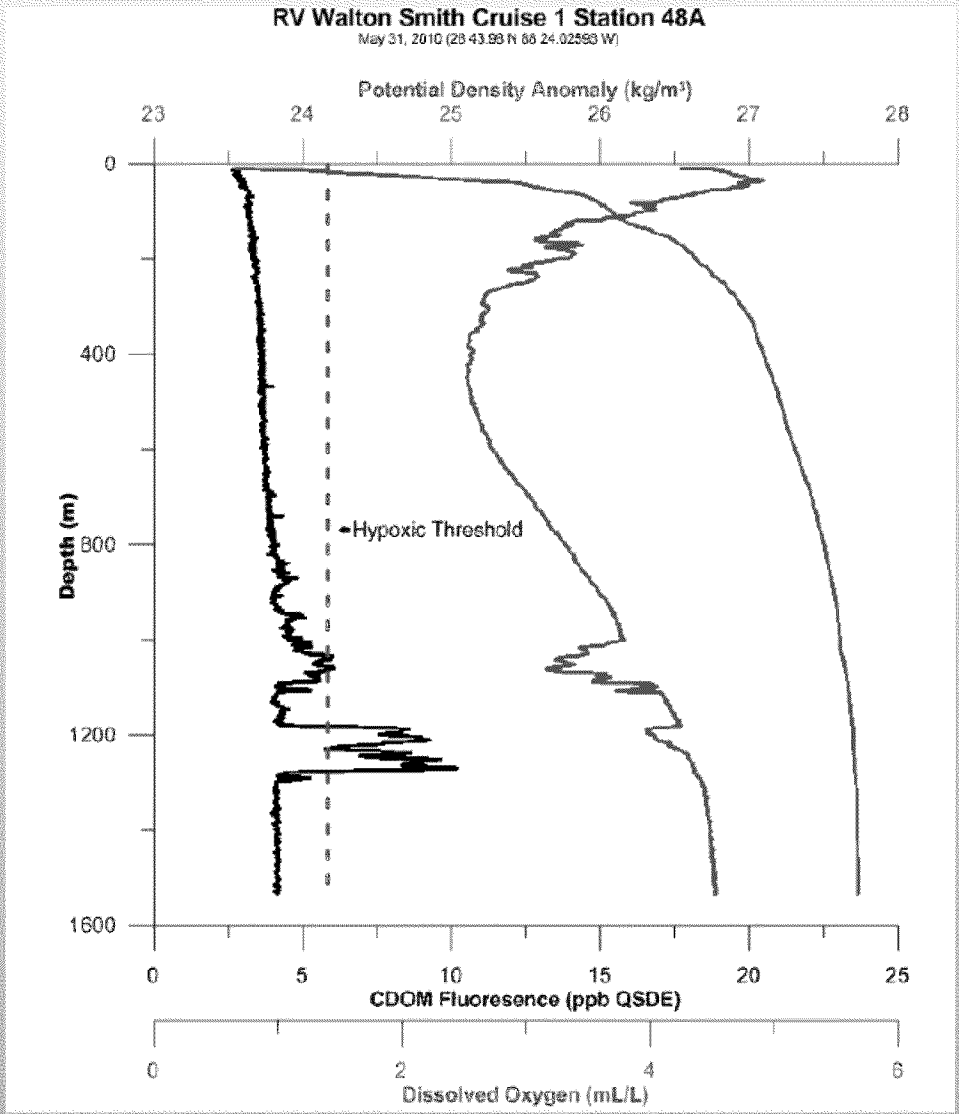
# Vertical profile showing 2 DO depressions coincident with fluorescence peaks



# Future Research Based on BP Spill

- Improvements in fluorometric monitoring of dispersed and non-dispersed oil plumes needed
  - Questions remain on optimum sensor configuration and NOM interference
  - 4-D mapping of dispersed oil plumes (leverage with NOAA)
  - Improved, innovative laser-based fluorometry (leverage with Canada DFO)
  - Better, faster analytical methods for measuring fate and transport of dispersed oil
- Develop green oil spill mitigation approaches for reduced toxicity and persistence in environment
- Better understanding of water-in-oil emulsions (mousse)
- Assessment of weathering effects on dispersion of oil
- Biodegradability of tar balls and other emulsions
- Exposure assessment scenarios for human and ecosystem effects
- Toxicity testing over many trophic levels
- Development of comparative risk assessments for sensitive species to inform risk management options





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# Application of SMART Protocol OSC Readiness, 2011

Harry L. Allen
US EPA/ERT

# What is SMART?

(From the NOAA Dispersant Applicator's Observation Job Aid)

- "Special Monitoring of Applied Response Technologies" (SMART) as a joint product of the USCG, NOAA, and EPA.
- SMART grew out of the Special Response Operational Monitoring Plan (SROMP) to avoid arguments over whether or not the dispersants were working.
- SMART: establishes a monitoring system for rapid collection and reporting of real-time, scientifically based information, in order to assist the Unified Command with decision-making during in situ burning or dispersant operations.
- SMART recommends monitoring methods, equipment, personnel training, and procedures that strike a balance between the operational demand for rapid response and the Unified Command's need for feedback from the field in order to make informed decisions.

# How do we use SMART?

- SMART applies particularly to the use of chemical dispersants and *in situ* burning as response alternatives.
- SMART is a decision-making tool during spill operations at a response and a planning tool where pre-approval is sought for burning or dispersant use.
- The SMART protocol has been updated and is available on the NOAA Website:
- http://response.restoration.noaa.gov
- Differences between NOAA and EPA arise over the interpretation of “response technology effectiveness.”

# How much dispersion is “effective” and will it cause aquatic toxicity?

- The NCP Product Schedule lists the effectiveness and toxicity of chemical countermeasures, but the RRT needs to approve their use.
- The minimum requirements for listing are dispersant effectiveness of 45% at the application rate of 1:20 Dispersant to Oil Ratio (DOR) in a swirling flask and a toxicity <1/10 LC50. The next slides are typical examples.
- Researchers have demonstrated effective dispersion in the lab at DORs of 1:25 and 1:100 using the new baffled flask test.
- The actual rate for the Deep Sea dispersant application at the well-head was about 1:195 (9 gpm/1,650 gpm).

## SUMMARY OF SUBPART J NOTEBOOK INFORMATION ON DISPERSANT FORMULATIONS

| Material Tested | Species | LC50 (ppm) | |
|---|---|---|---|
| COREXIT® EC9500A | Menidia beryllina | 25.20 96-hr | |
| | Mysidopsis bahia | 32.23 48-hr | |
| No. 2 Fuel Oil | Menidia beryllina | 10.72 96-hr | |
| | Mysidopsis bahia | 16.12 48-hr | |
| COREXIT® EC9500A & | Menidia beryllina | 2.61 96-hr | |
| No. 2 Fuel Oil (1:10) | Mysidopsis bahia | 3.40 48-hr | More toxic when dispersed. |
| Reference Toxicant (SDS) | Menidia beryllina | 7.07 96-hr | |
| | Mysidopsis bahia | 9.82 48-hr | |

## SWIRLING FLASK DISPERSANT EFFECTIVENESS TEST FOR COREXIT 9500A TEST WITH SOUTH LOUISIANA (S/L) AND PRUDHOE BAY (P/B) CRUDE OILS

| Oil Effectiveness (%) | % |
|---|---|
| Prudhoe Bay Crude | 45.3% |
| South Louisiana Crude | 54.7% |
| Average of Prudhoe Bay and South Louisiana Crudes | 50.0% |

# Use SMART to know you are getting effective dispersion?

- SMART Tier 1 relies on visual observation of dispersant effectiveness by trained observers.
- SMART Tier 2 employs field analytical techniques such as fluorometry (referenced to background), turbidity, droplet size distribution, conductivity, temperature, and depth (CTD) to estimate dispersion.
- SMART Tier 3 requires sampling and analysis to determine what oil fractions are being dispersed, whether the emulsions are physical or chemical, and whether there are toxic chemicals in the emulsion. Lab work is usually required. Dissolved oxygen is also considered a Tier 3 analyte, but electronic DO meters need lab calibration.

# Estimating Initial Oil on the Water

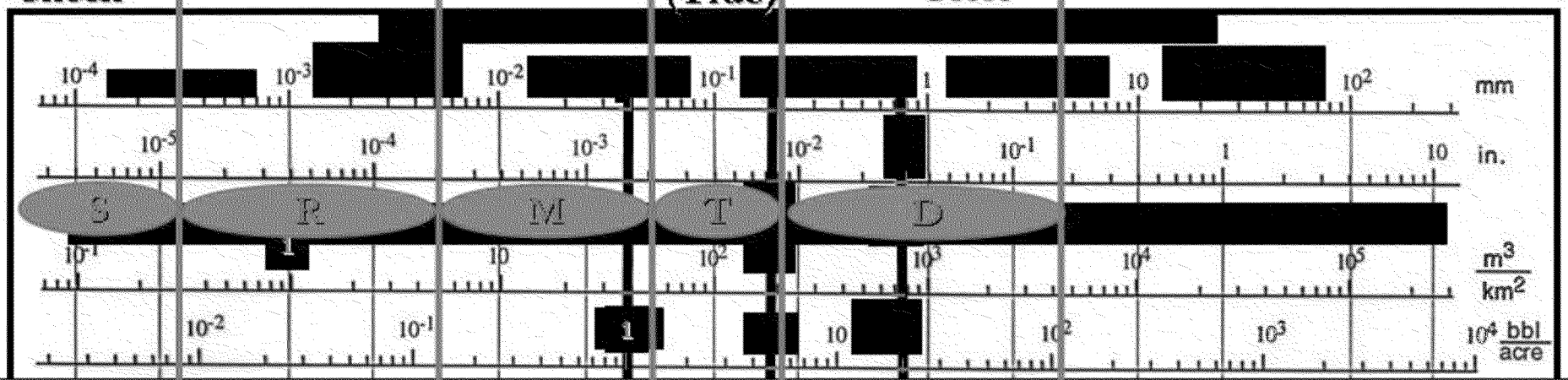
- It is an important first step to estimate the amount of oil on the surface in order to determine the required dispersant loading or to predict the feasibility of *in situ* burning.
- Al Allen of Spiltec has created an elegant oil thickness estimation system. Using this and an estimate of the area of oil coverage, we can calculate oil volume on the surface. If we have made an initial estimate before dispersant application, the relative degree of dispersion can be estimated as closely as by any other means.

# Visual Estimation of Oil Thickness & Quantity

Note:
1 μm = 1 $m^3/km^2$
≈ 0.026 bbl/acre

Color Code

| Silvery Grey Sheen | Rainbow | Metallic | Trans. Dark (True) | Dark (True) Color |
|---|---|---|---|---|
| 0.3 μm<br>$3 \times 10^{-4}$ mm<br>$1.2 \times 10^{-5}$ in. | 5 μm<br>$5 \times 10^{-3}$ mm<br>$2 \times 10^{-4}$ in. | 50 μm<br>$5 \times 10^{-2}$ mm<br>$2 \times 10^{-3}$ in. | 200 μm<br>$2 \times 10^{-1}$ mm<br>$8 \times 10^{-3}$ in. | 4,000 μm<br>4 mm<br>0.16 in. |




| 0.1 μm | 1 μm | 10 μm | 100 μm | 1000 μm |
|---|---|---|---|---|
| $10^{-4}$ mm | $10^{-3}$ mm | $10^{-2}$ mm | $10^{-1}$ mm | 1 mm |
| $4 \times 10^{-6}$ in. | $4 \times 10^{-5}$ in. | $4 \times 10^{-4}$ in. | $4 \times 10^{-3}$ in. | $4 \times 10^{-2}$ in. |

If not bounding, use as "nominal" mid-range values for each code #

Crude Oils Appear Dark ("True") in Color

Warm Stable

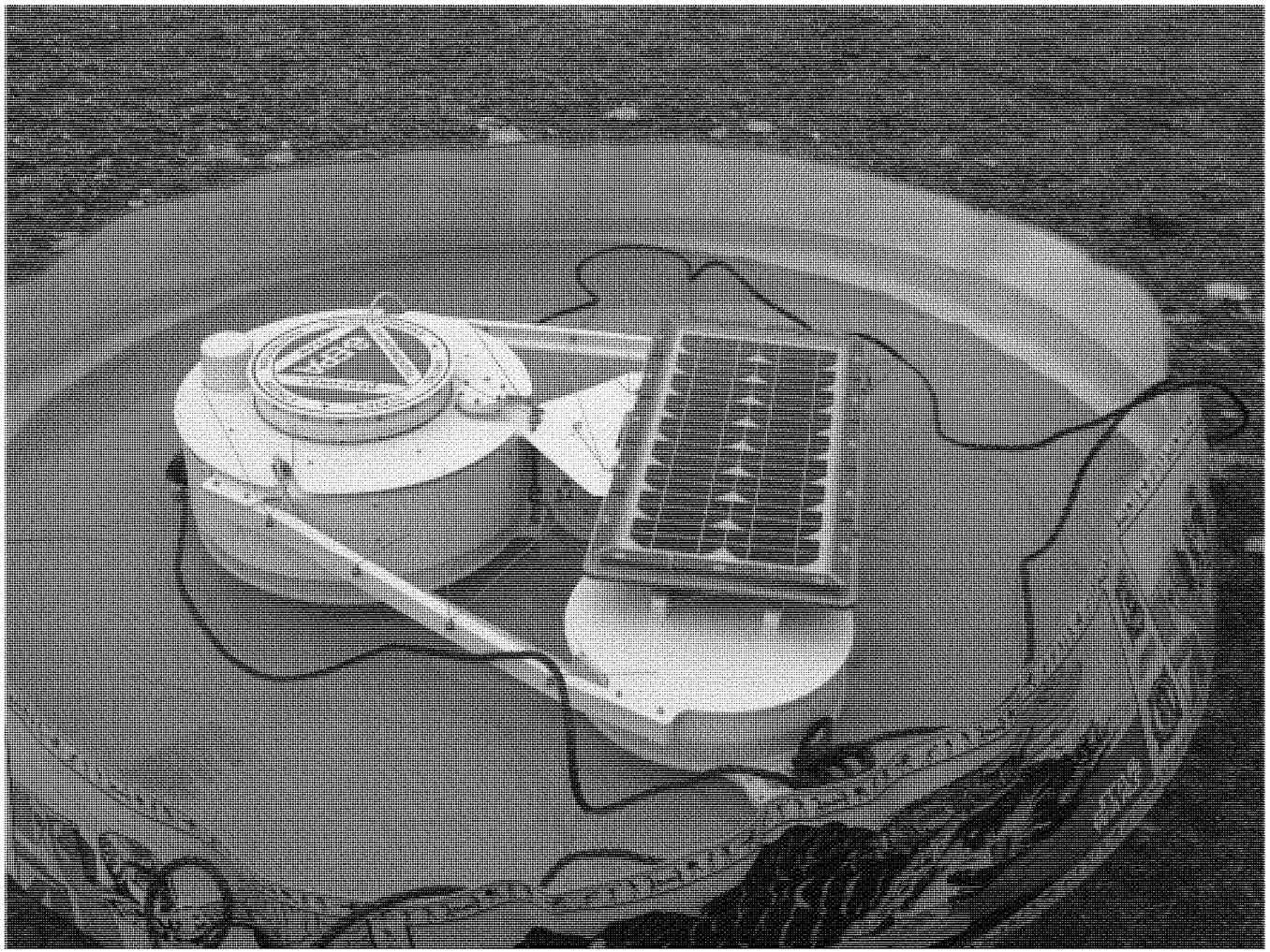
Emulsions

Cold Stable

Dr. Alan A. Allen, Spiltec

# The Leakwise Detector “Waverider” by GE Systems

May be used to measure the thickness of floating or emulsified oil remotely. Then it emails  and texts this information to Command.



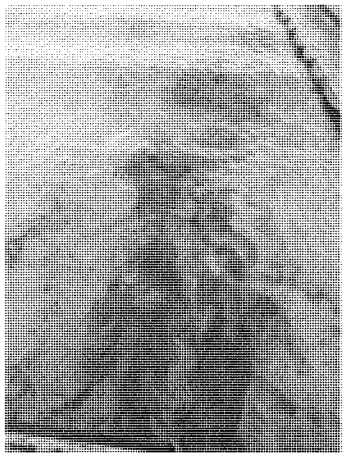
# Standardizing SMART Tier 1

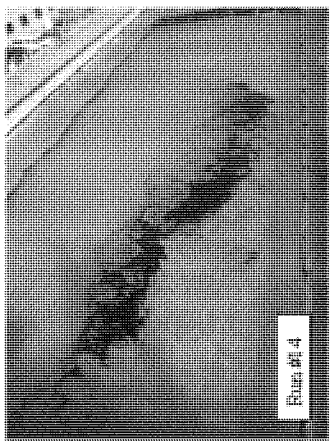
- Visual assessment of oil slick and oil in surface waters:
  - Trained observers may be hard to find.
  - Attempts to standardize observation and reporting of visual dispersion observations
  - Assesses ONLY initial break up of slick into dispersed oil droplets
  - Remember that dilution of the dispersant may allow the oil to resurface after a few hours. Think “Terminator 2.”

| Lewis Four Point Effectiveness Scale | |
|---|---|
| **Effectiveness rating** | **Description[a]** |
| 1 | No visible evidence of dispersion |
| 2 | Some evidence of partial dispersion |
| 3 | Moderate and incomplete dispersion |
| 4 | Rapid and complete dispersion |

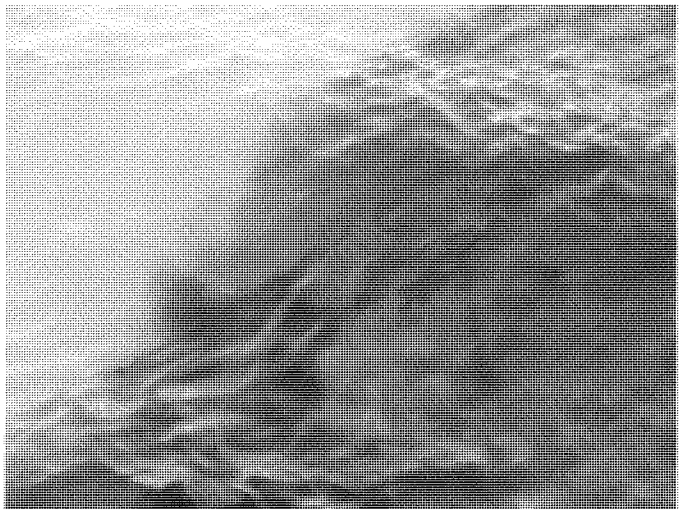
a. Based only on behavior of oil in first 15 minutes after dispersant added and agitated by waves.

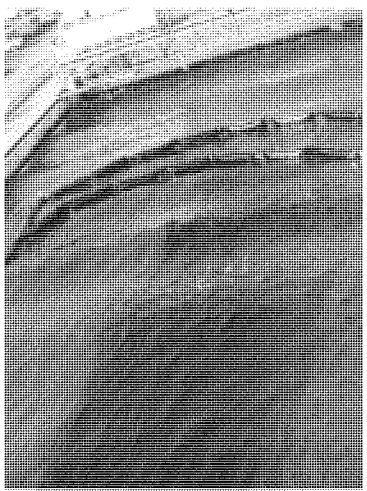
Visual Effectiveness = 1



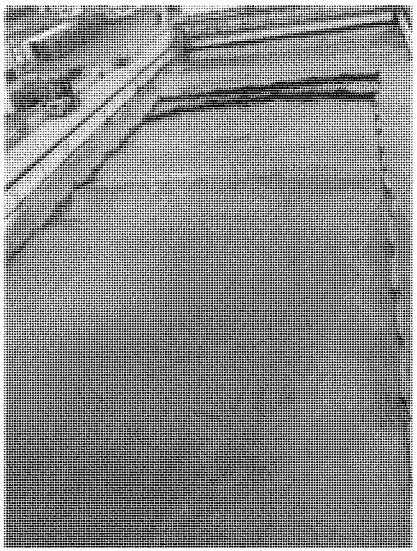



Visual Effectiveness = 3





Visual Effectiveness = 4



# SMART Tier 2 - Fluorometry

- Dissolved unsaturated and aromatic hydrocarbons, when excited by light waves at 280-320 nm, emit photons (fluoresce) at characteristic wavelengths. Aromatic hydrocarbons emit at about 340 nm; saturated hydrocarbons at about 445 nm. The size of the signal relates to the concentration of each fraction.
- Tier 2 SMART procedure makes use of this characteristic. Deploying a fluorometer by boat, the monitoring team samples at a depth of 1 to 2 m along transects through sections of the slick before and after dispersant spraying.

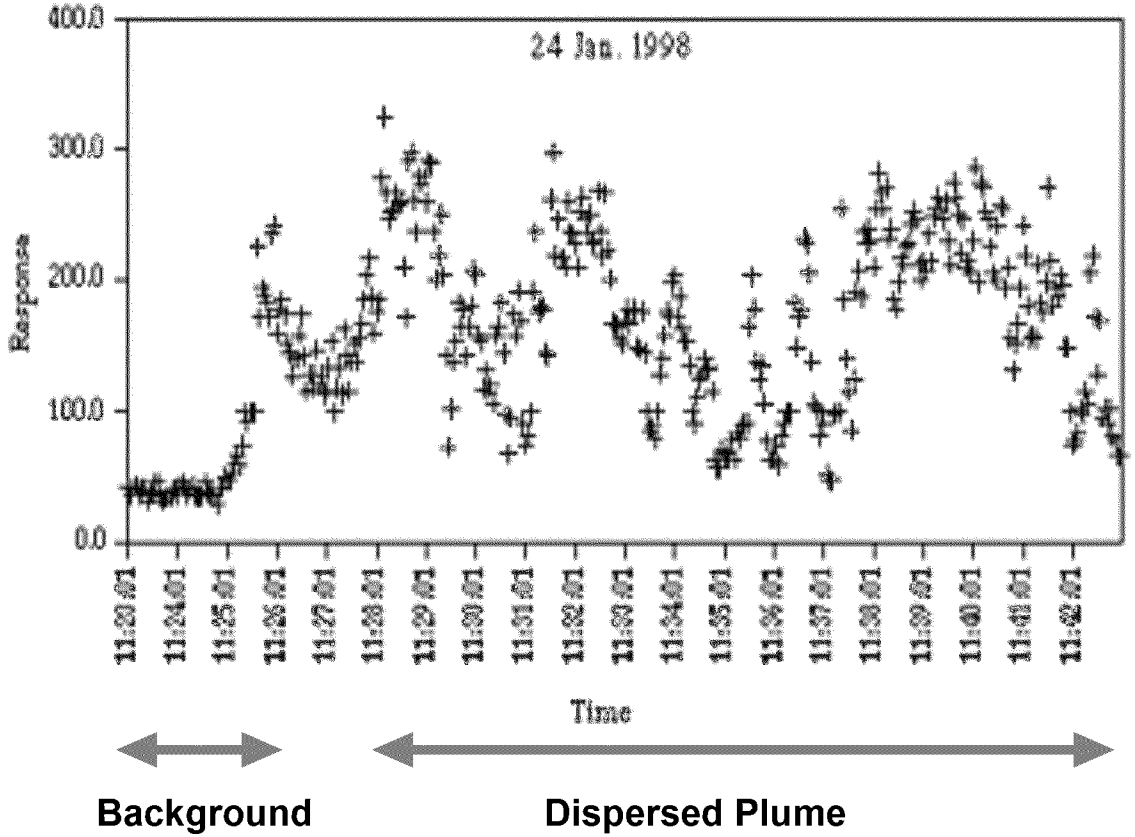
# SMART Tier 2 – Fluorometry (cont'd.)

- Vessel tows fluorometer outside the oil plume and bisects the oil plume to get a baseline of natural dispersability.
- Aircraft applies dispersant over target area.
- Dispersant applications are judged to be effective if fluorometer readings under treated slicks are at least 5 times greater than under untreated slicks (i.e., under the slick prior to treatment).
- Grab samples are taken from the water stream or by Kemmerer at predetermined intervals for post-event calibration of the fluorometer using the actual oil spilled and for Tier 3 analysis if required.

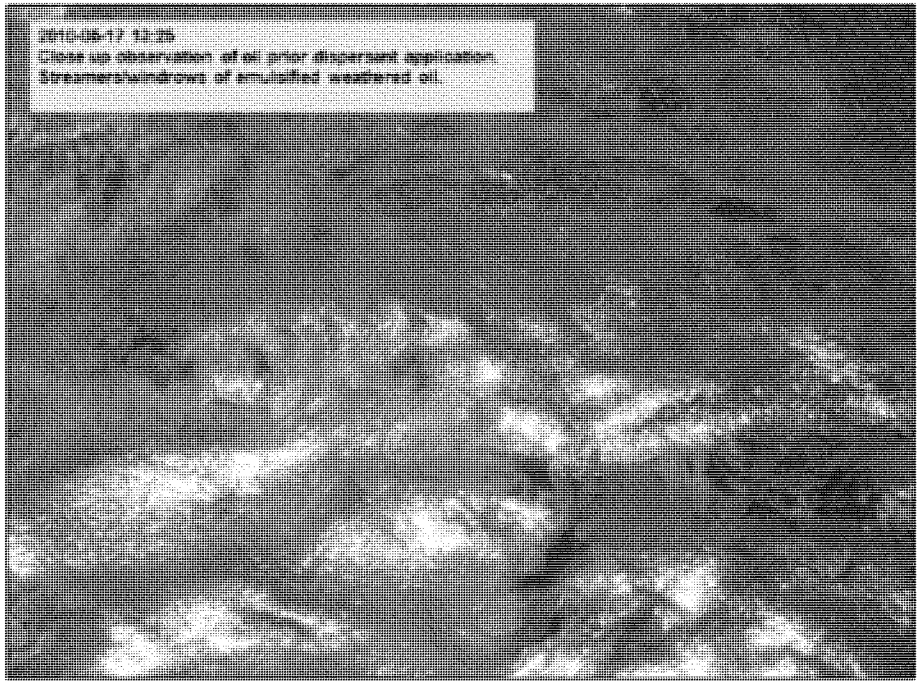
# Steps for SMART Tier 2 - Fluorometry

- Vessel tows fluorometer thirty minutes after dispersant application at a starting position outside the oil plume and bisects the plume to determine the effectiveness of the dispersant application.
- Vessel tows fluorometer sixty minutes after dispersant application at a starting position outside the oil plume and bisects the plume to determine the effectiveness of the dispersant application.

# Ideal Surface Application of Dispersant

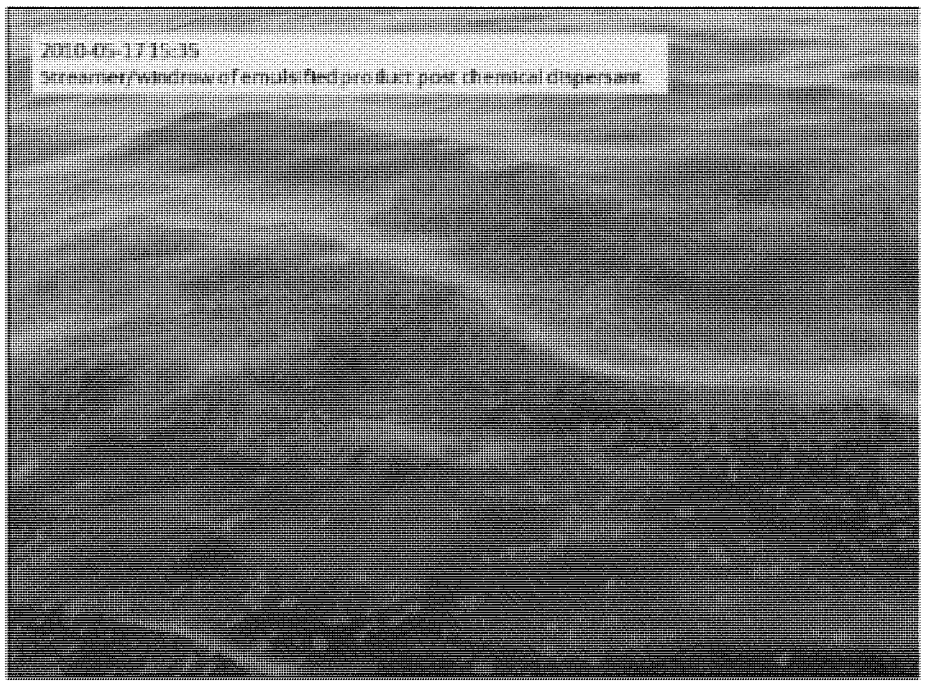



"Ideal" Fluorometry Trace from Historical Record




What does it look like?

**Data to date show dispersant effectiveness is consistent with our expectations**



# Choosing your Weapons for SMART Tier 2

- Fluorometers
- Particle Counters
- Bubble Size Indicators

Turner AU 10 Fluorometer
The “Old”

Turner Cyclops C6 Fluorometer
The “New”

# Turner C3 Fluorometer

"Weapon of Choice" in the Gulf

The Turner C3 fluorometer (excitation wavelength of 320 nm and emission wavelength of 400-600 nm) was towed by boat through the dispersed oil plume at 1-m and 2-m depths to make measurements of the dispersed oil plume both within the plume and up to 50-m outside the plume.

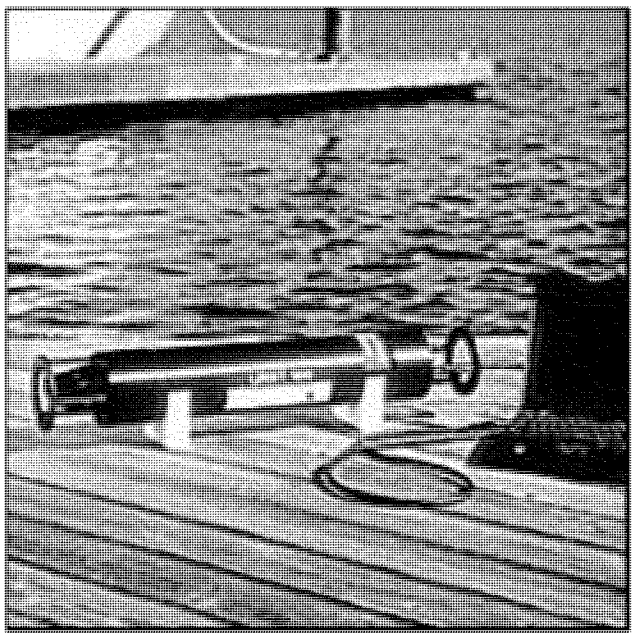
# BUBA Buster / Wetstar x GPS

- In-situ fluorescence detector combined with GPS
- Simple setup
- Continuous monitoring along transects
- Provides spatially-registered estimates of concentrations

TAMU FL3 and LISST-100X at Ohmsett

# Sequoia Particle and Particle-size Analyser

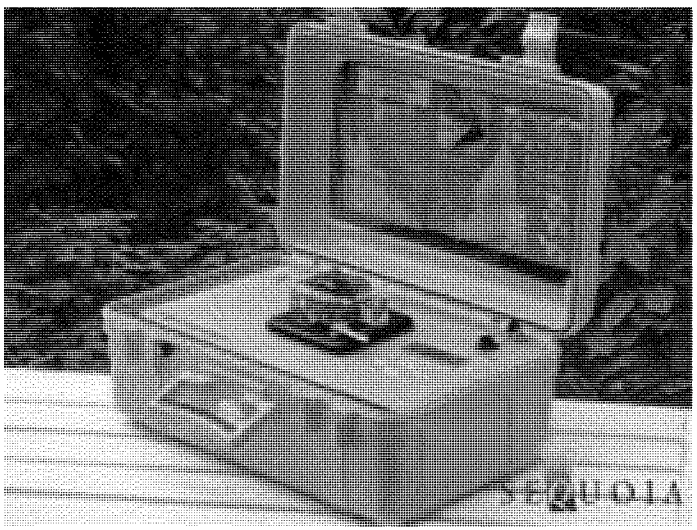
- Measures both oil droplet abundance and particle size in the range of 2.5 – 500 microns
- In-situ measurement
- Little set up needed
- Requires “blank”
- Needs clean water standard
- Continuous monitoring on transects
- Laser *In-Situ* Scattering and Transmissometry (LISST) instrument.



**LISST–100X Type-C**

# Sequoia On-Board Analysis

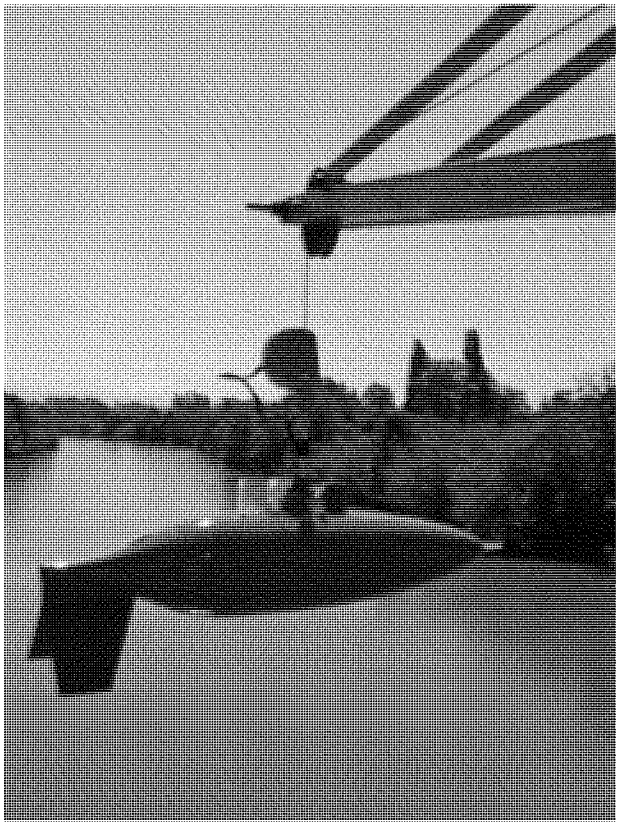
- Ex-situ particle-size analyser
- Analytical capability of LISST 100, but in ex-situ format
- Continuous monitoring
- Requires pump on effluent side
- Requires “blank”
- Amenable to post-calibration



**Sequoia Steam-Side**

# Sequoia Towable

- Towable in-situ particle-size analyser
- Analytical capability of LISST 100, but in easily towable
- Designed for freshwater,but could be set up form marine use

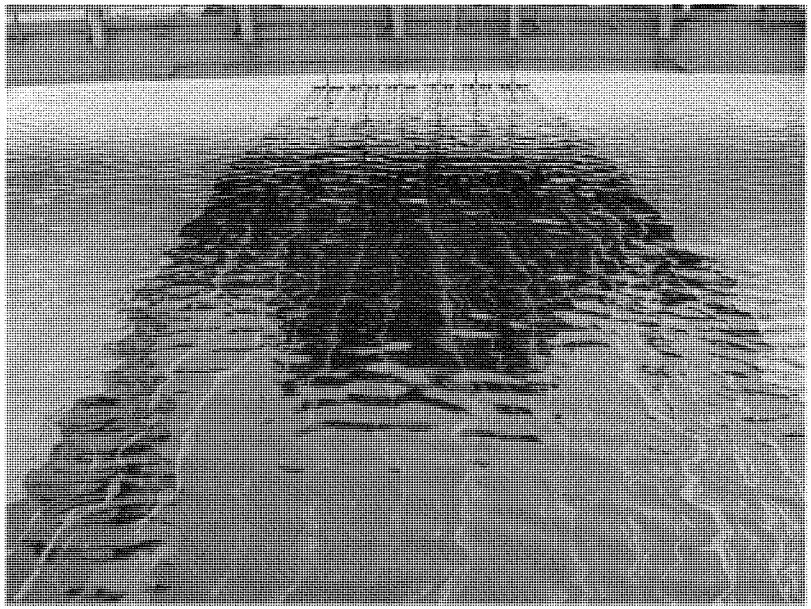


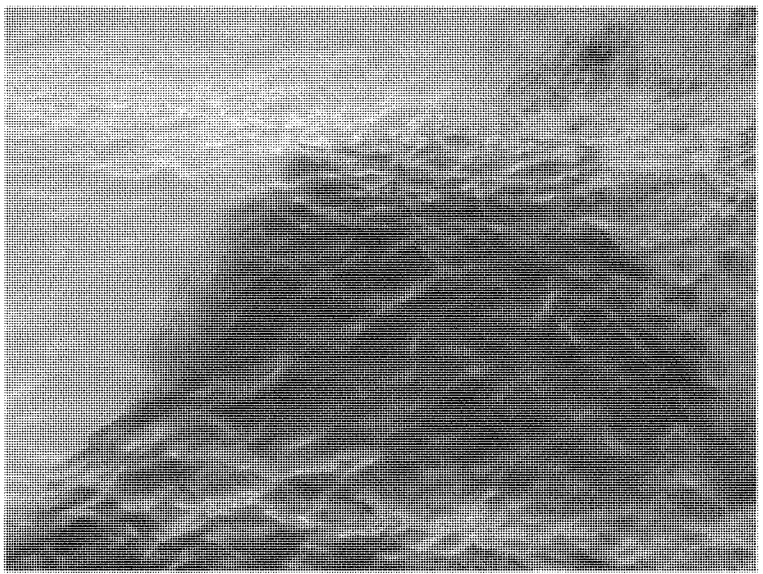
**Sequoia SL**

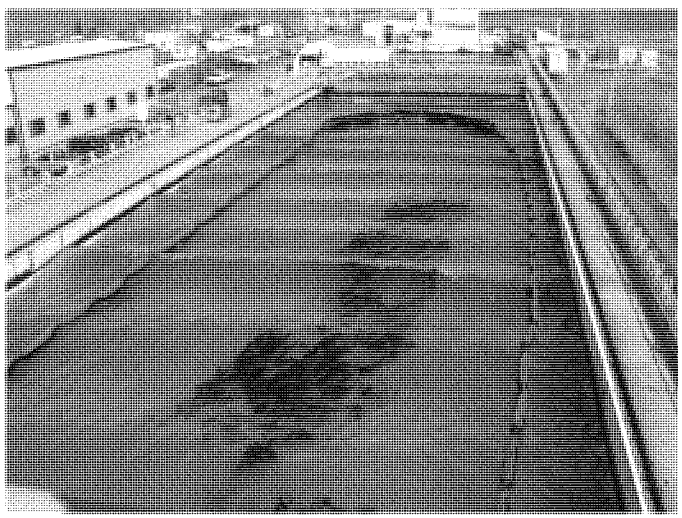
# Summary of New Items
## Based on a presentation by Ken Trudel

| Instrument | Pre-Deployment Engineering & Peripherals | On-Site Set-up and Calibration | Weight | Cost | Global Positioning System |
|---|---|---|---|---|---|
| Turner 10AU | Pump, power,hose, down-rigger | Assembly, calib w dye and/or oil | 35 lb Fluorometer only | $ 16 K | Extra |
| BUBA Buster | In-situ | Little set up; No user calib.; Diesel Standard | | $ 4K/ Unit Based on CDOM cost | Included |
| LISST -100X | In-situ | Blank | 25 lbs | $ 29.5 K/ Unit | Extra |
| LISST Stream-Side | Pump, power,hose, down-rigger | Blank | 15 lbs | $ 15K/ Unit | Extra |
| LISST SL | In-situ | Blank | 35 lbs | $ 35K/ Unit | Extra |
| Turner C3 | In-situ | Intuitive Calibration | 3.6 lbs | $ 8.5 K | Extra |

# Testing of Equipment at OHMSETT



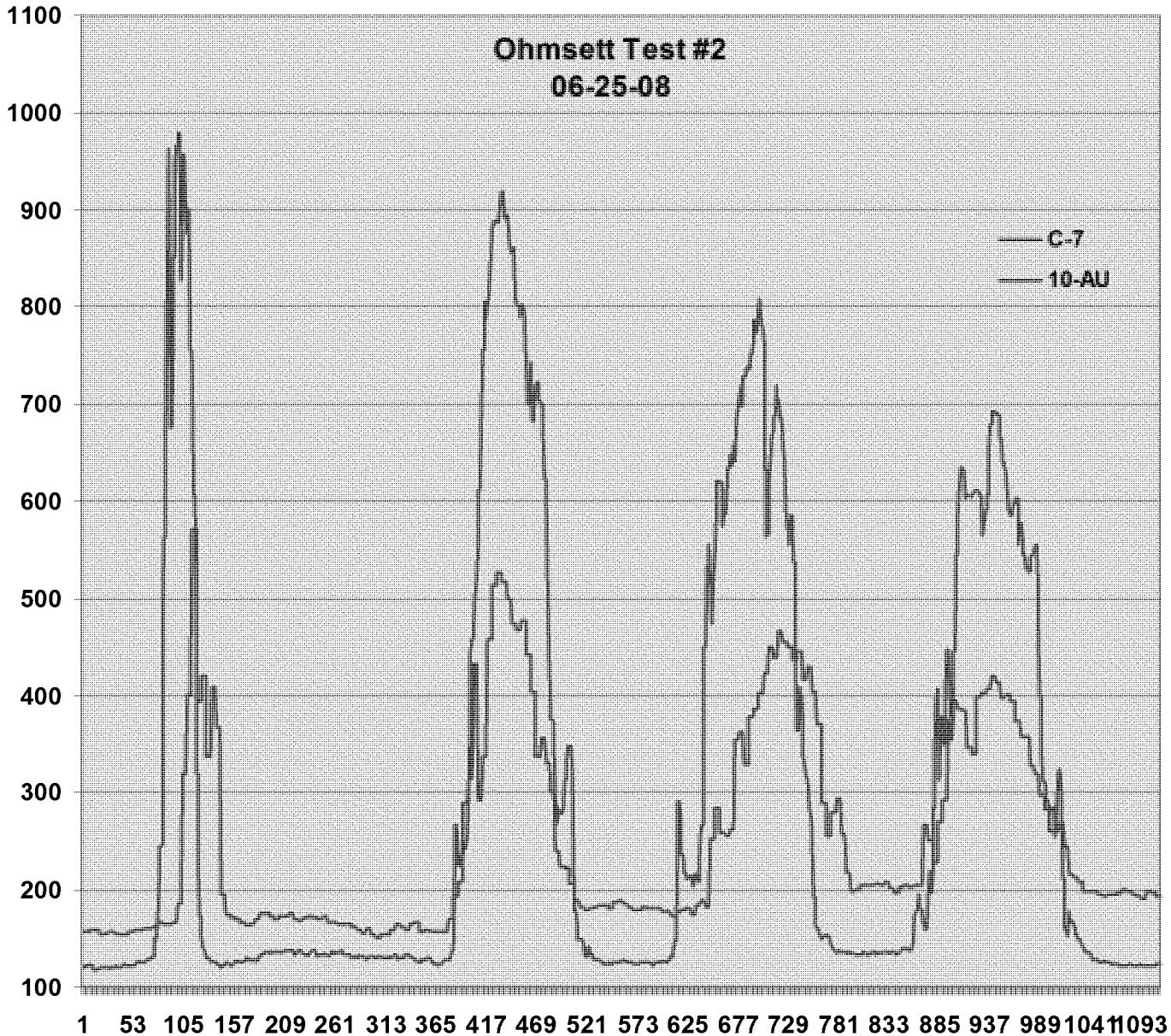




# Results of AU-10/Cyclops Comparison at OHMSETT June 2008

**Brian Parscal <brian@cleanislands.org>**

- Two tests were conducted on June 25th.
- The 10-AU was calibrated according SMART protocol standards while the C-7 was set to collect raw data on the medium gain setting. That most likely explains the difference in amplitude between the two.
- The C-7 (Cyclops) can detect dissolved oil in sea water and considering its ease of use, may be a good candidate for the SMART program.

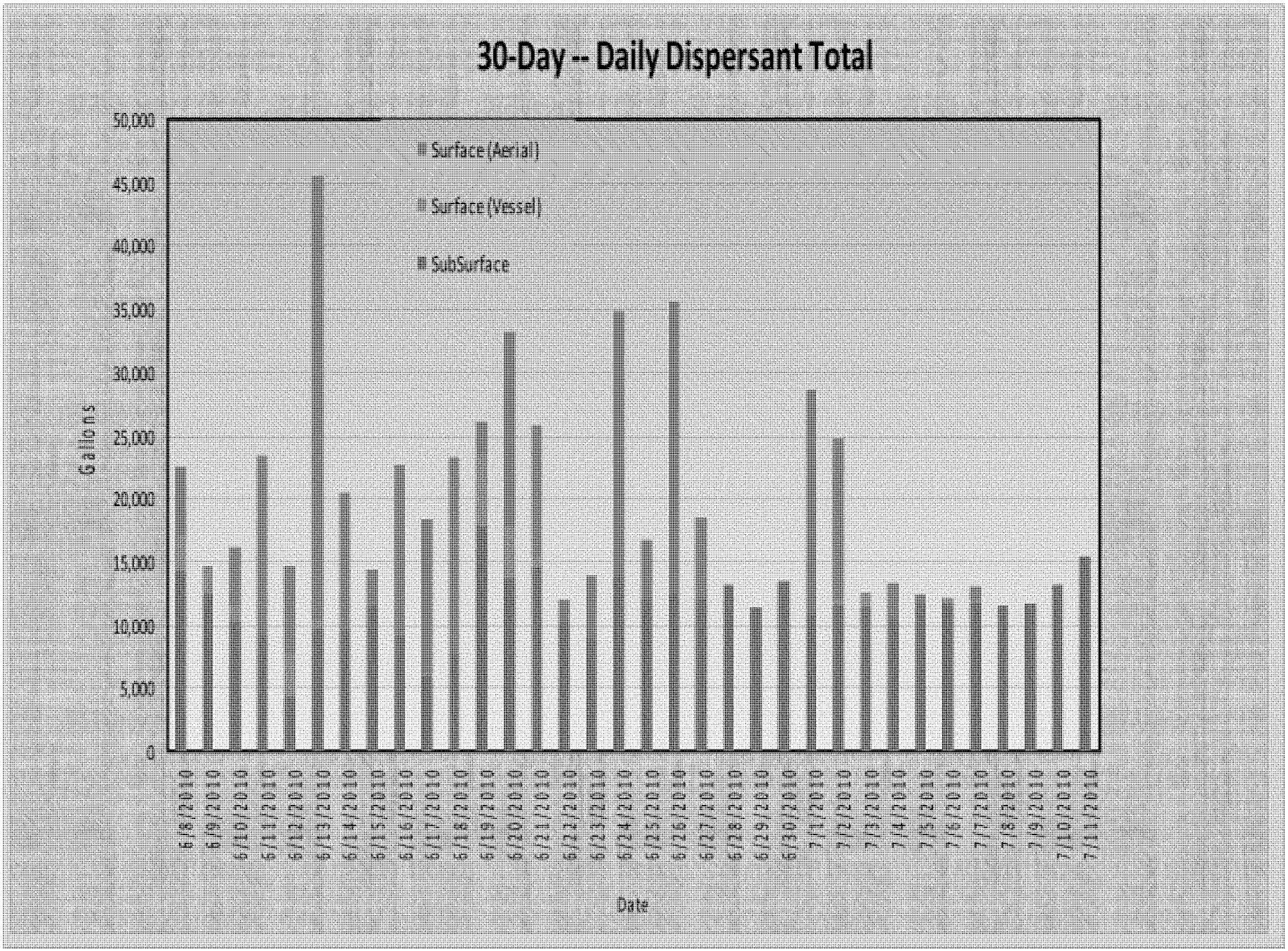

Ohmsett Test #2
06-25-08
C-7
10-AU
1100
1000
900
800
700
600
500
400
300
200
100
1 53 105 157 209 261 313 365 417 469 521 573 625 677 729 781 833 885 937 989 1041 1093

# Pros and Cons of Tier 2

- Fluorometry using a fixed wavelength is useful since it responds well to the dispersant concentration.
- Dispersed oil concentration and droplet size distribution is a very good indicator of dispersion effectiveness.
- Fluorometry cannot determine how the oil fingerprint is changing and what oil fractions actually are being dispersed; multiple emission wavelengths would be a better indicator of dispersed fractions.
- Small droplet size (<70 microns on nm) indicates good dispersion, and research indicates very fine (20 nm) particles are a strong indicator of chemical dispersion at moderate turbulence.
- Under the turbulent conditions of an expanding HC gas release at 152 atm, a stable emulsion might be generated mechanically.

# Surface Dispersant Application at the Deepwater Horizon

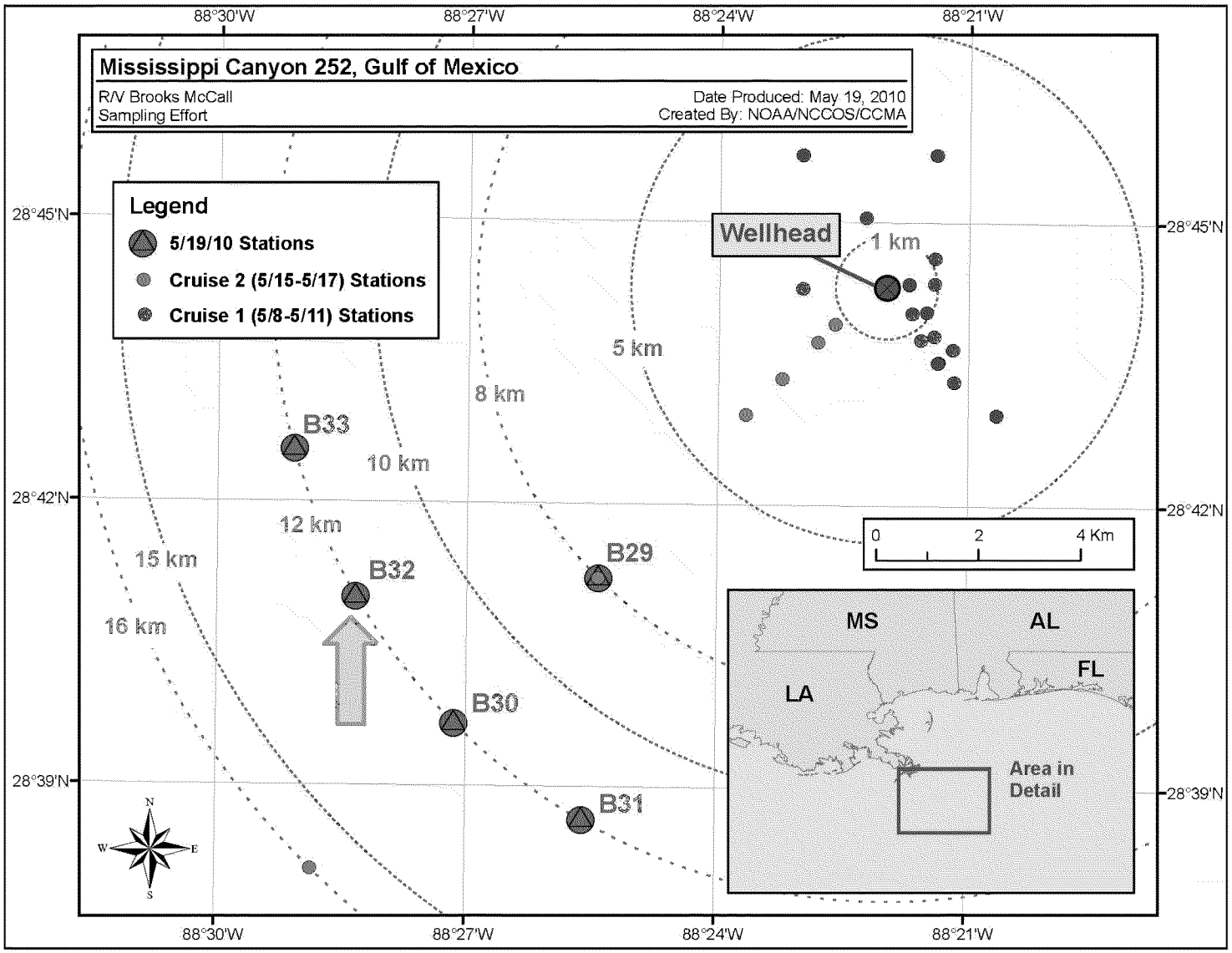
- Per RRT guidance application occurs >3 miles offshore and water depth of > 10 meters
- Applied primarily via aircraft
- As of 07/12/10
  - 404 sorties flown
  - 975,038 gallons sprayed
  - 305 sq miles covered (195,008 acres)


30-Day -- Daily Dispersant Total
Surface (Aerial)
Surface (Vessel)
SubSurface
Gallons
50,000
45,000
40,000
35,000
30,000
25,000
20,000
15,000
10,000
5,000
0
6/8/2010
6/9/2010
6/10/2010
6/11/2010
6/12/2010
6/13/2010
6/14/2010
6/15/2010
6/16/2010
6/17/2010
6/18/2010
6/19/2010
6/20/2010
6/21/2010
6/22/2010
6/23/2010
6/24/2010
6/25/2010
6/26/2010
6/27/2010
6/28/2010
6/29/2010
6/30/2010
7/1/2010
7/2/2010
7/3/2010
7/4/2010
7/5/2010
7/6/2010
7/7/2010
7/8/2010
7/9/2010
7/10/2010
7/11/2010
Date

# Field Application
# DWH Oil Spill
# Brooks-McCall Cruise
# May 19, 2011

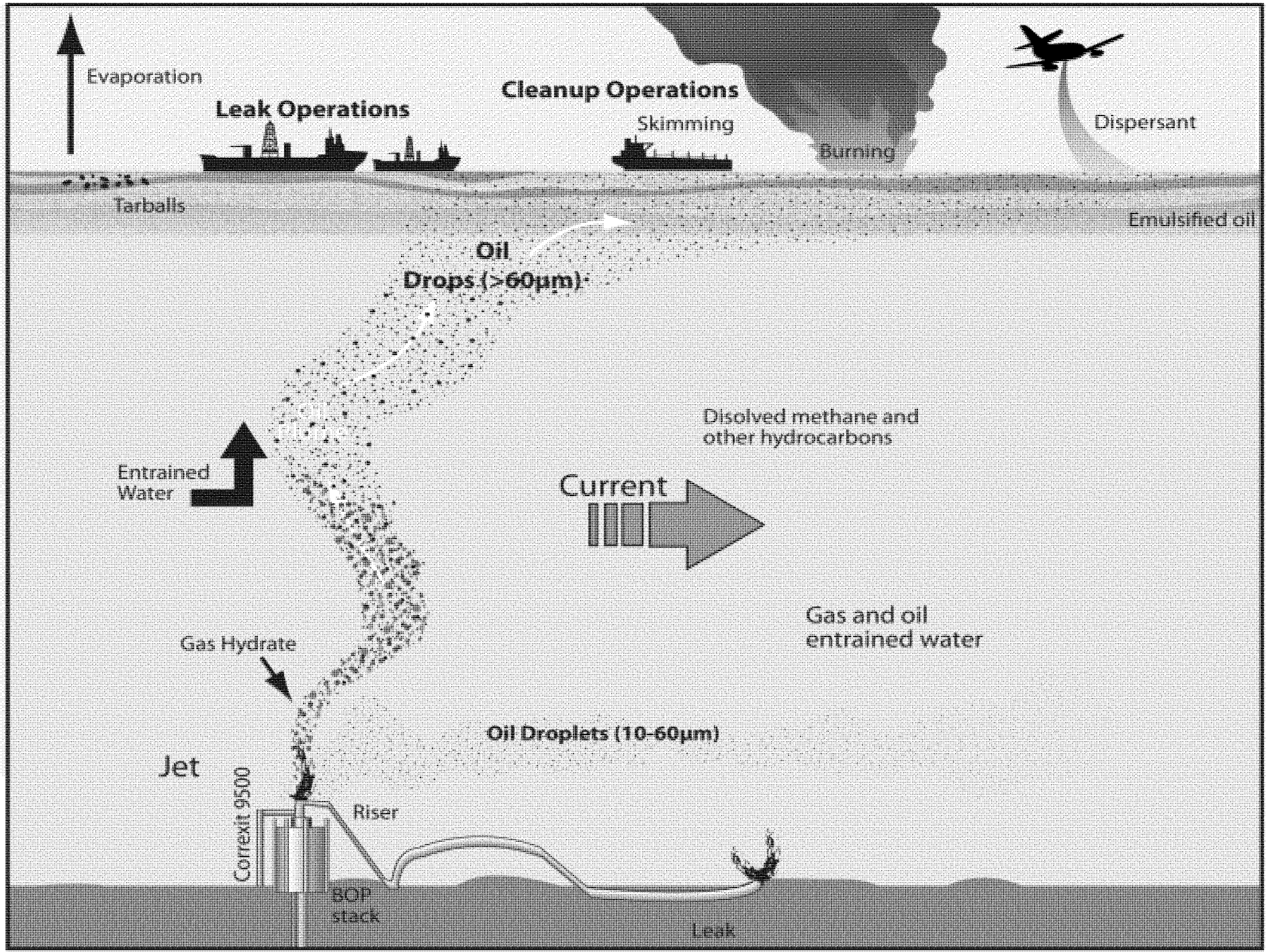
## Conductivity, Temperature, Density (CDT) Data plus Fluorometry Traces

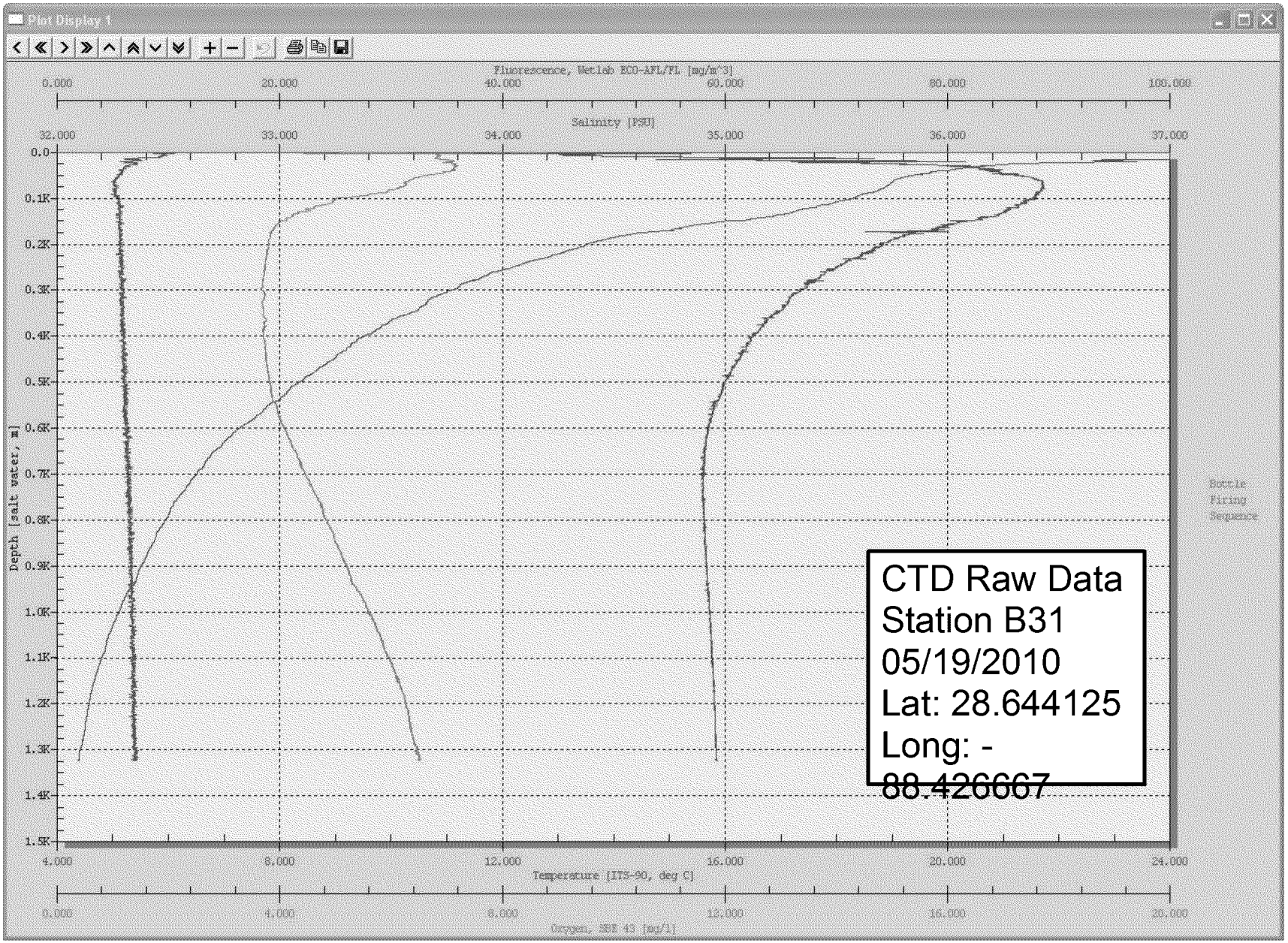
# Sampling Locations

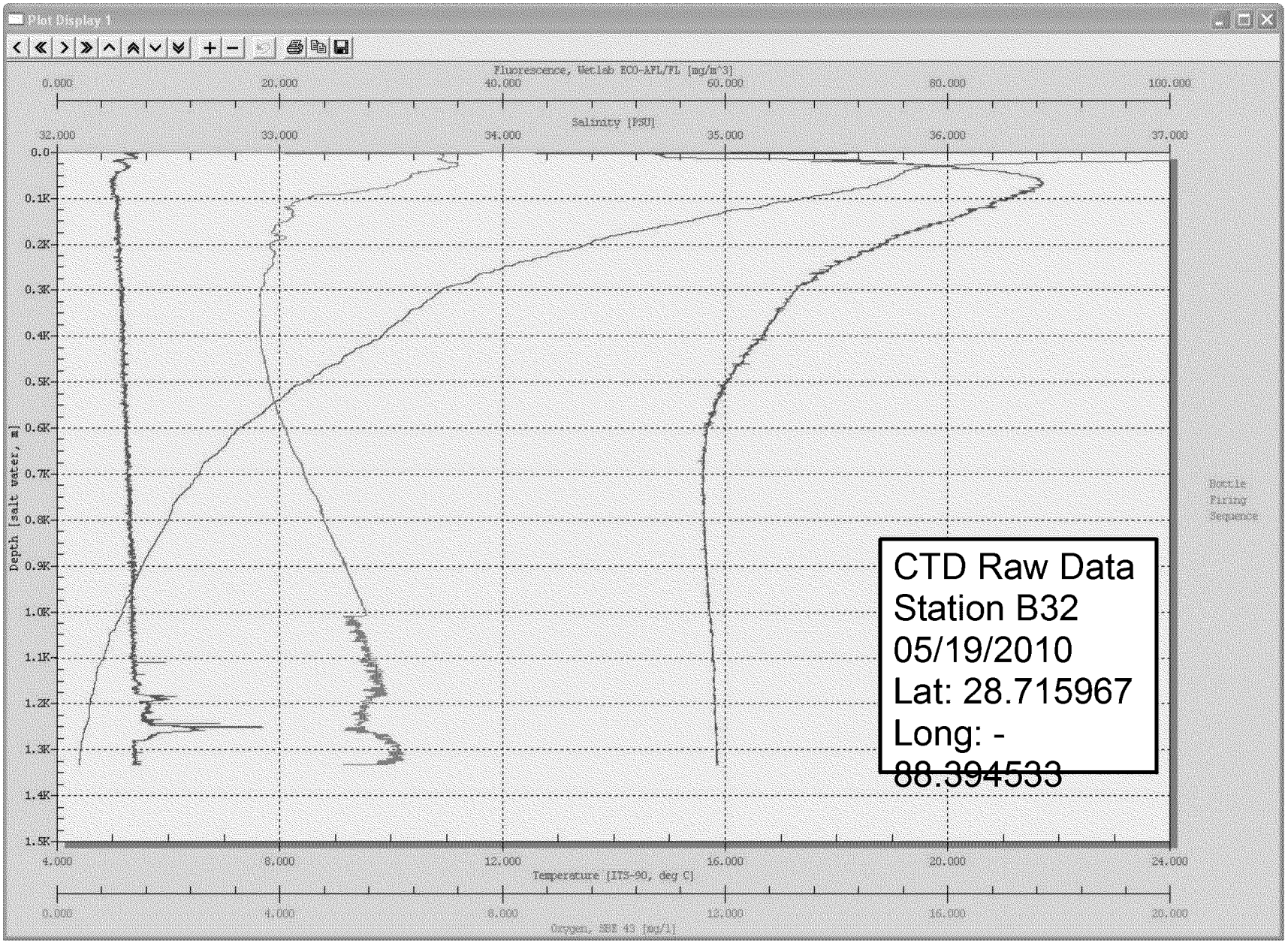


# On-Board Fluorometry

- Two fixed wavelength UV fluorometers were employed in tandem to determine Fluorescence Intensity Ratios (FIRs).
- One fluorometer was equipped with a pair of wavelength filters allowing excitation at 280 nm and emission at 340 nm.
- The second fluorometer was equipped with the same 280 nm excitation filter and a longer (445 nm) wavelength.
- FIRs were then calculated from fluorescence intensity at 340 nm divided by intensity at 445 nm.

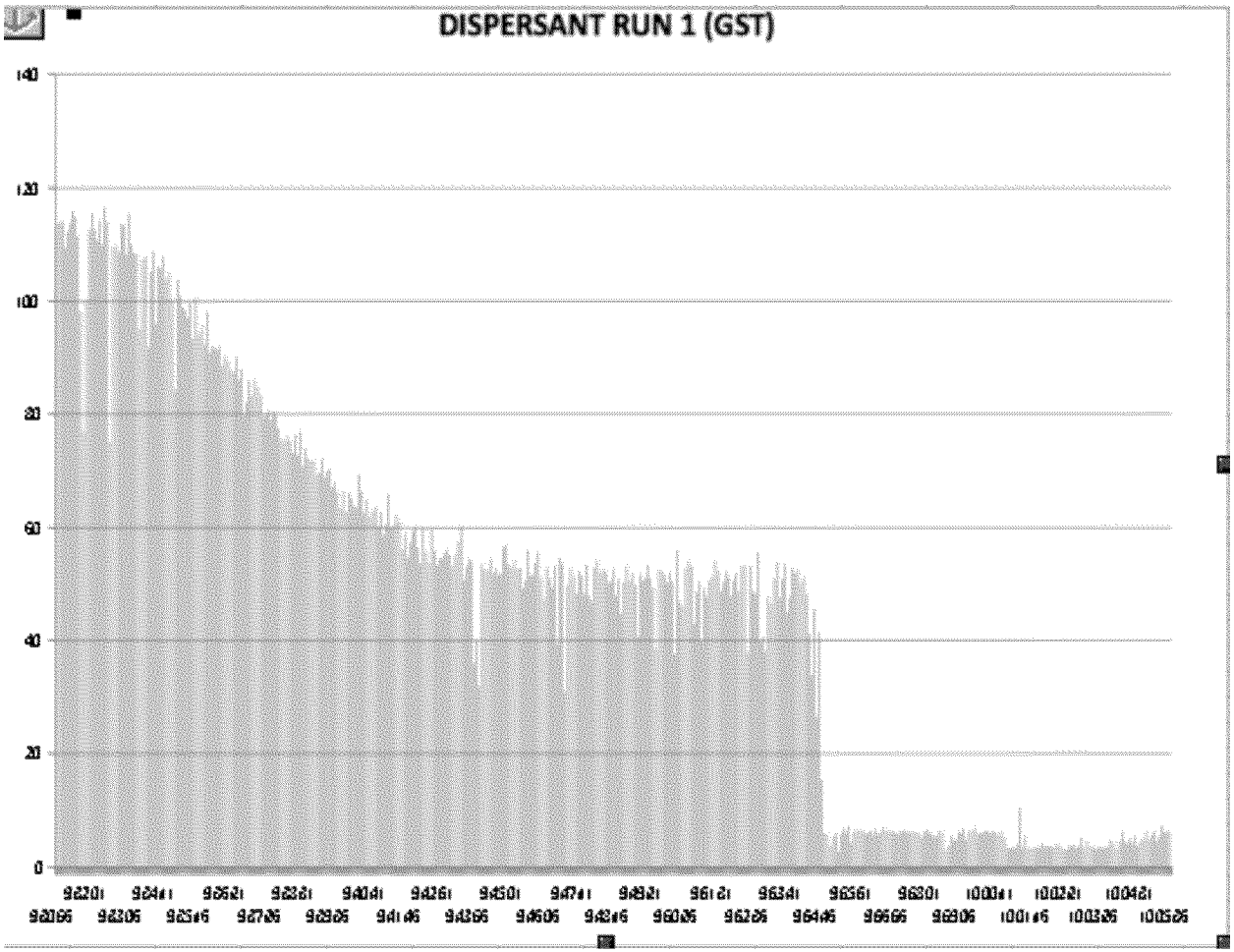

Evaporation
Leak Operations
Cleanup Operations
Skimming
Burning
Dispersant
Tarballs
Emulsified oil
Oil
Drops (>60µm)
Disolved methane and
other hydrocarbons
Entrained
Water
Current
Gas and oil
entrained water
Gas Hydrate
Oil Droplets (10-60µm)
Jet
Correxit 9500
Riser
BOP
stack
Leak


Plot Display 1
Fluorescence, Wetlab ECO-AFL/FL [mg/m^3]
0.000
20.000
40.000
60.000
80.000
100.000
Salinity [PSU]
32.000
33.000
34.000
35.000
36.000
37.000
Depth [salt water, m]
0.0
0.1K
0.2K
0.3K
0.4K
0.5K
0.6K
0.7K
0.8K
0.9K
1.0K
1.1K
1.2K
1.3K
1.4K
1.5K
Bottle Firing Sequence
CTD Raw Data
Station B31
05/19/2010
Lat: 28.644125
Long: -88.426667
4.000
8.000
12.000
16.000
20.000
24.000
Temperature [ITS-90, deg C]
0.000
4.000
8.000
12.000
16.000
20.000
Oxygen, SBE 43 [mg/l]

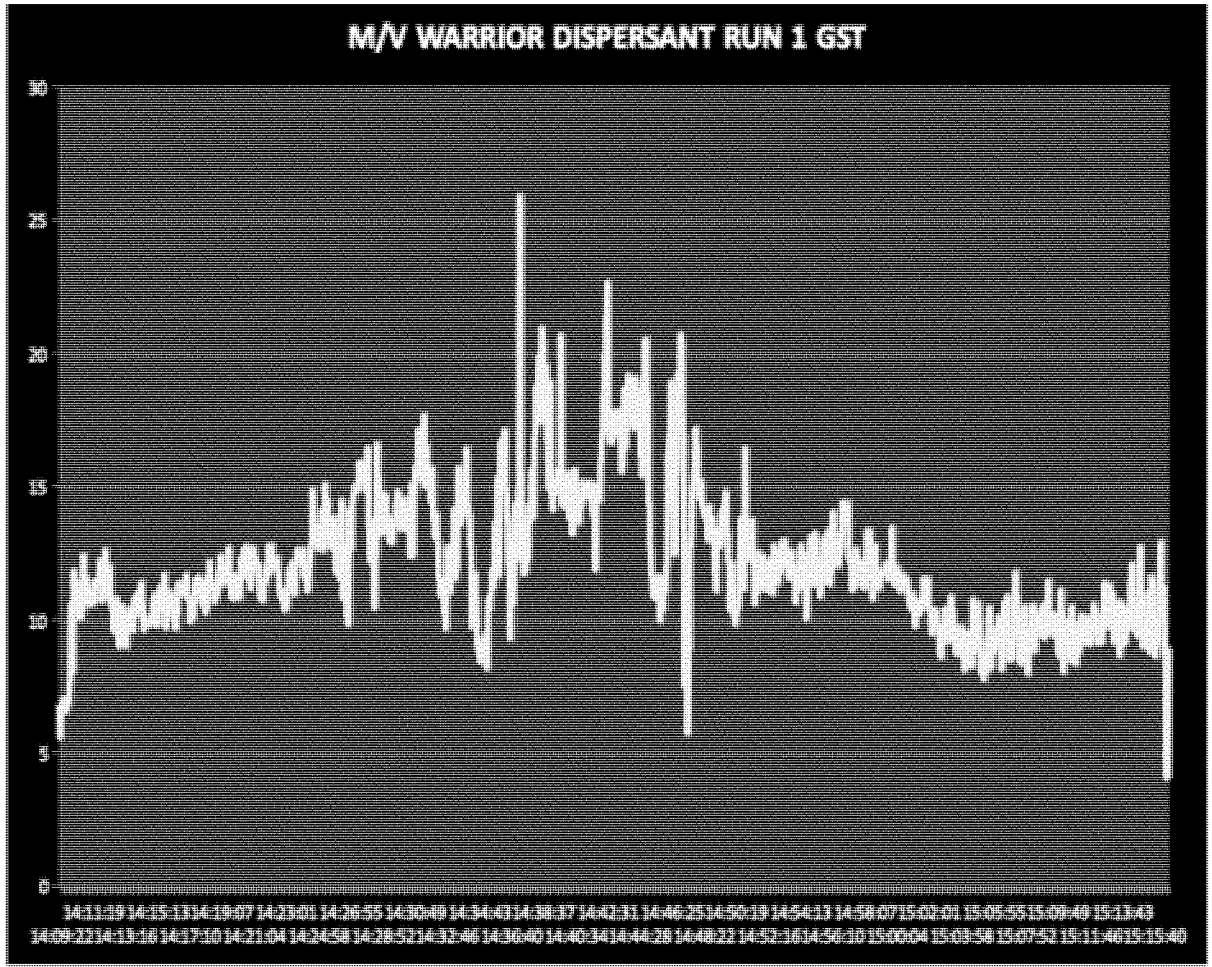

Plot Display 1
Fluorescence, Wetlab ECO-AFL/FL [mg/m^3]
0.000
20.000
40.000
60.000
80.000
100.000
Salinity [PSU]
32.000
33.000
34.000
35.000
36.000
37.000
Depth [salt water, m]
0.0
0.1K
0.2K
0.3K
0.4K
0.5K
0.6K
0.7K
0.8K
0.9K
1.0K
1.1K
1.2K
1.3K
1.4K
1.5K
Bottle Firing Sequence
CTD Raw Data
Station B32
05/19/2010
Lat: 28.715967
Long: -88.394533
4.000
8.000
12.000
16.000
20.000
24.000
Temperature [ITS-90, deg C]
0.000
4.000
8.000
12.000
16.000
20.000
Oxygen, SBE 43 [mg/l]

# SMART Tier 2
# Monitoring of Surface Application of Dispersant

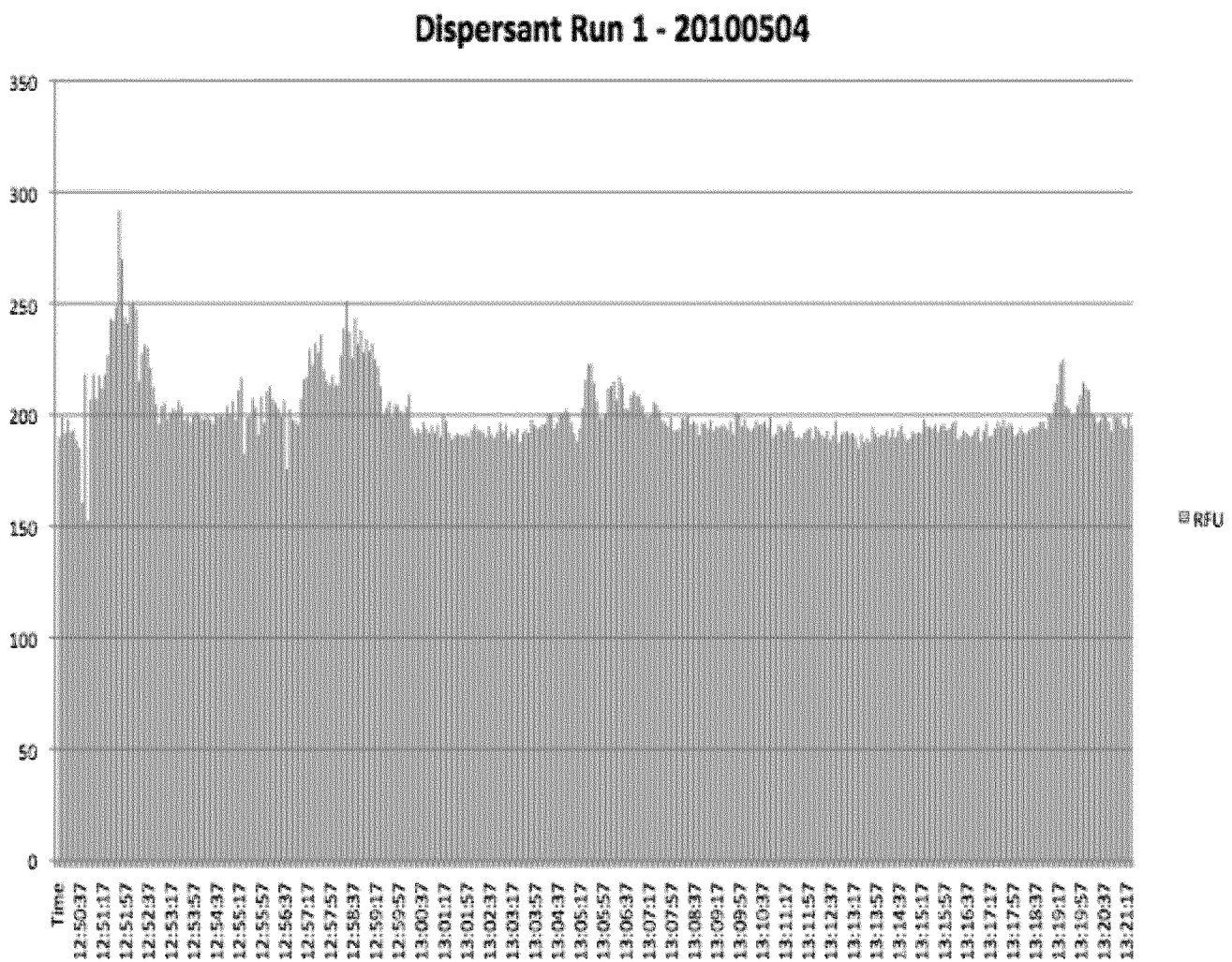
- A set of results was submitted to the HQ Science Group for assessment.
- The following 5 figures were used by EPA to determine that surface application of dispersant was not effective.
- The 6th figure is a good example of a fluorometry trace which compares mechanical and chemical dispersion near the surface.



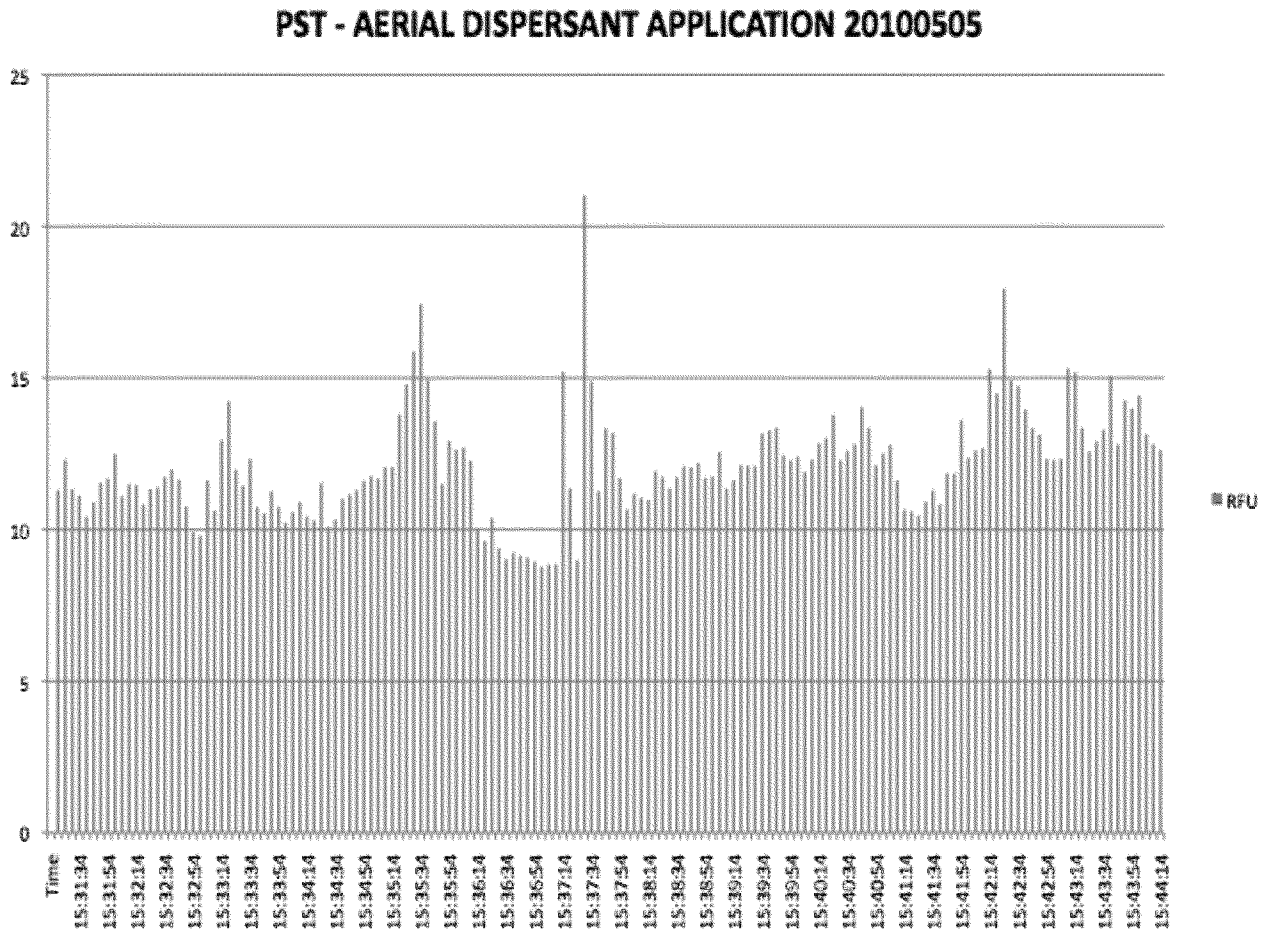

Increase of Fluorometry Reading >10x
(Almost 30x at Mid-plume)
Successful Application 4/28/2010




Unsuccessful Dispersant Application 4/28/2010

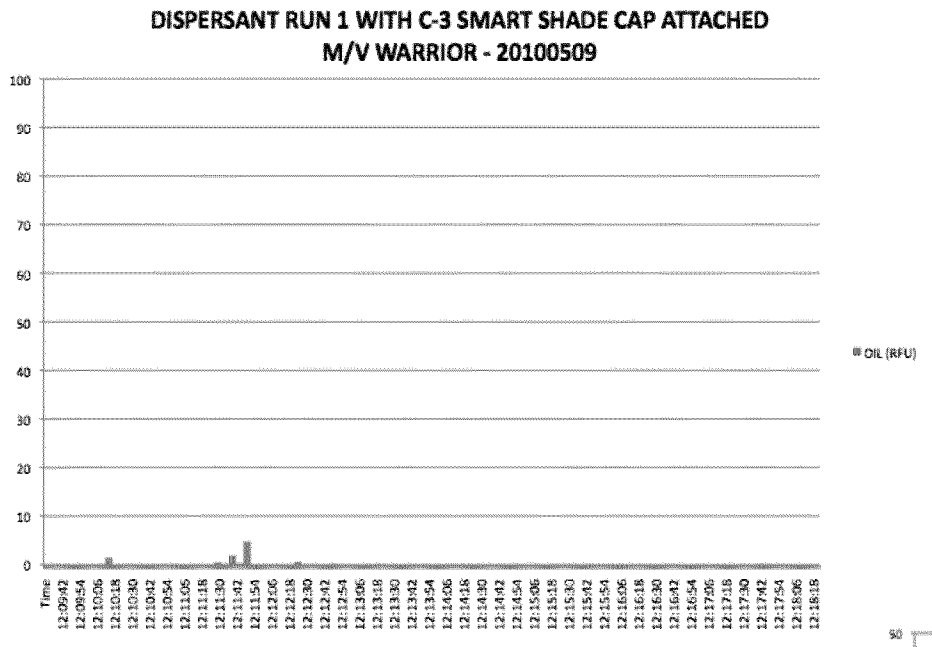


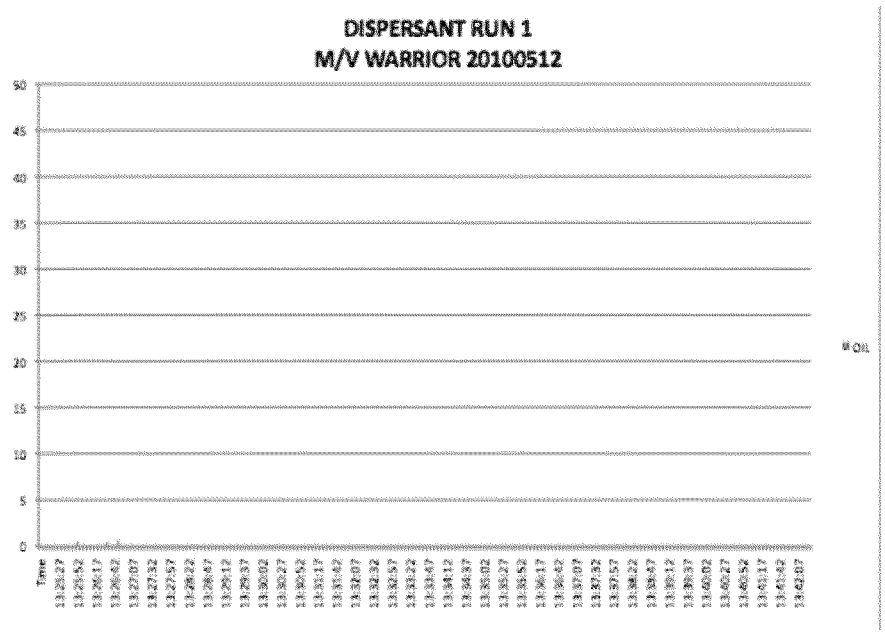

Unsuccessful Dispersant Application 5/4/2010

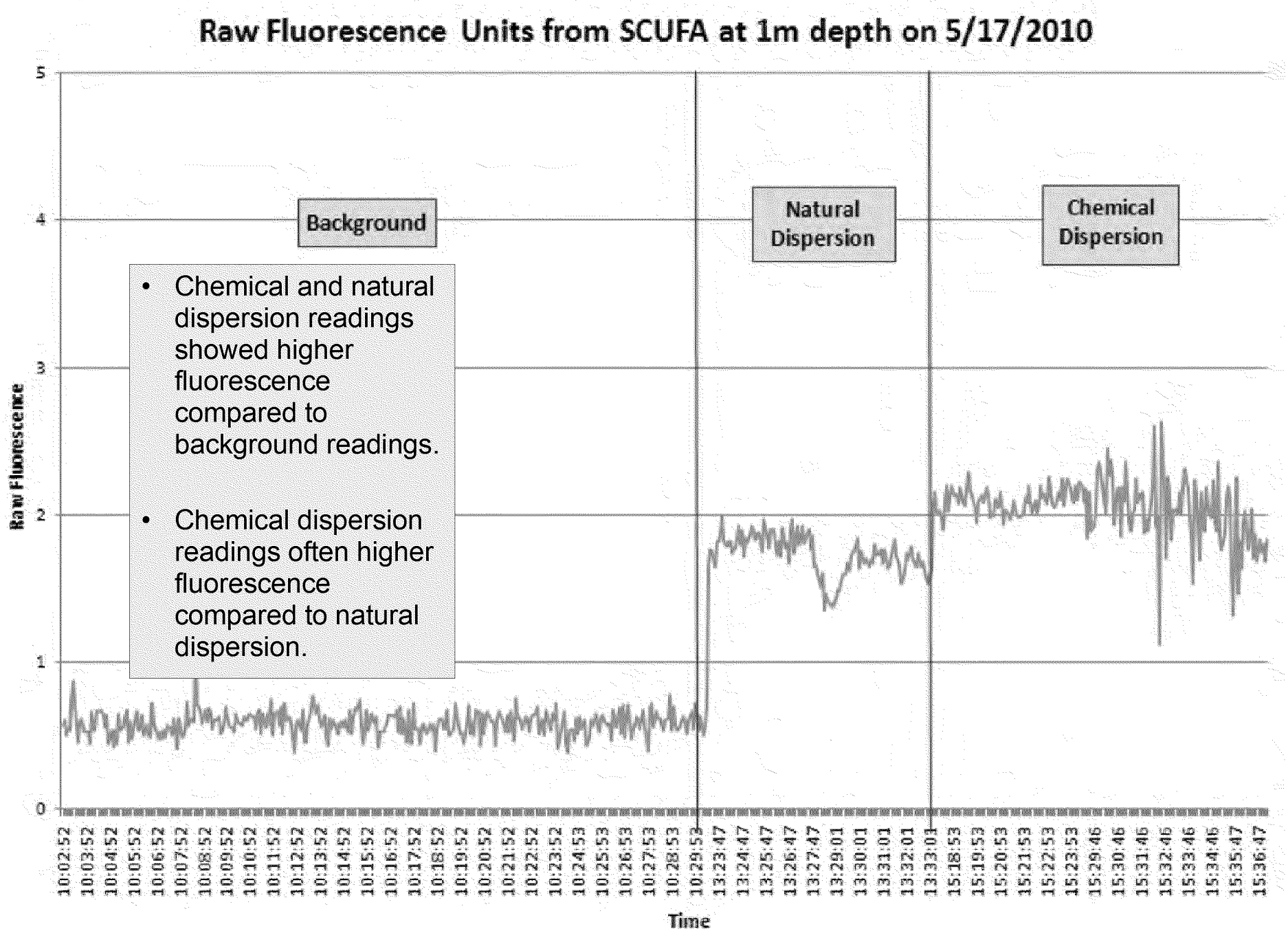



Unsuccessful Dispersant Application 5/5/2010

# Incomplete Fluorometry Data Runs of 5/9-10/2010




Raw Fluorescence Units from SCUFA at 1m depth on 5/17/2010
Background
Natural Dispersion
Chemical Dispersion
• Chemical and natural dispersion readings showed higher fluorescence compared to background readings.
• Chemical dispersion readings often higher fluorescence compared to natural dispersion.
Raw Fluorescence
0
1
2
3
4
5
10:02:52
10:03:52
10:04:52
10:05:52
10:06:52
10:07:52
10:08:52
10:09:52
10:10:52
10:11:52
10:12:52
10:13:52
10:14:52
10:15:52
10:16:52
10:17:52
10:18:52
10:19:52
10:20:52
10:21:52
10:22:52
10:23:52
10:24:53
10:25:53
10:26:53
10:27:53
10:28:53
10:29:53
13:23:47
13:24:47
13:25:47
13:26:47
13:27:47
13:29:01
13:30:01
13:31:01
13:32:01
13:33:01
15:18:53
15:19:53
15:20:53
15:21:53
15:22:53
15:23:53
15:29:46
15:30:46
15:31:46
15:32:46
15:33:46
15:34:46
15:35:47
15:36:47
Time

# So now we can judge for ourselves as to the "effectiveness" of dispersant application.

- How effective was the dispersant in removing the oil from the environment?
- How effective was the dispersant in reducing the environmental impact?
- In other words, where is the rest of the oil and dispersant and what kind of toxic residuals can we expect?

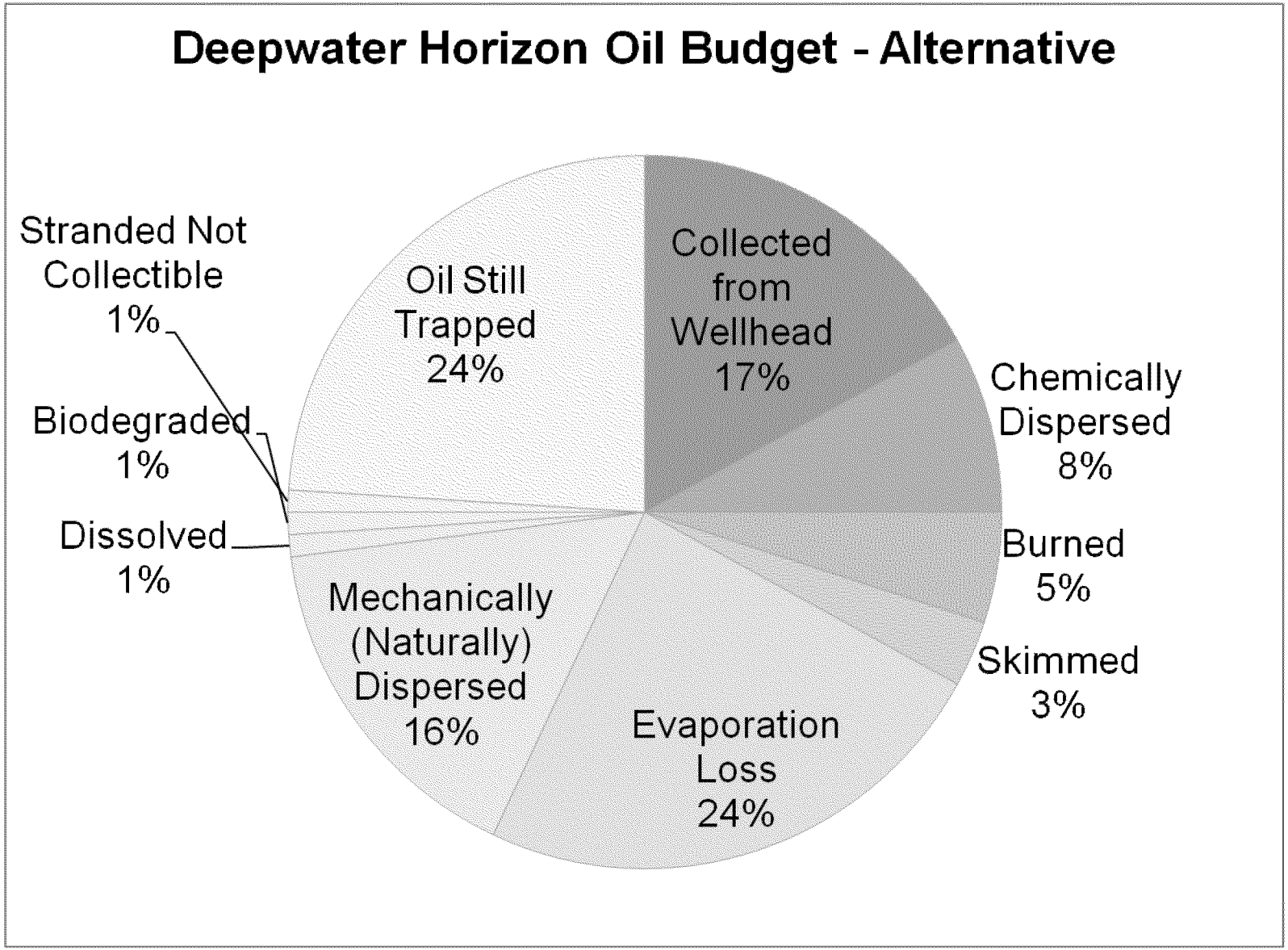
# Deepwater Horizon Oil Budget Quantities

ERT Edition of NOAA/USGS Budget

| | Fraction | MG |
|---|---|---|
| Collected from Wellhead | 0.17 | 35.0 |
| Chemically Dispersed | **0.08** | **16.5** |
| Burned | 0.05 | 10.3 |
| Skimmed | 0.03 | 6.2 |
| Evaporation Loss | 0.24 | 49.4 |
| Mechanically (Naturally) Dispersed | **0.16** | **32.9** |
| Dissolved | 0.01 | **2.1** |
| Biodegraded | 0.01 | 2.1 |
| Stranded Not Collectible | **0.01** | **2.1** |
| Oil Still Trapped | **0.24** | **49.4** |
| Residual Still in the Gulf System | 0.50 | **100.8** |

Actually, a 25% recovery is remarkable, and if we count the 8% chemically dispersed, 33% mitigation is quite a feat!!

# Modified Oil Budget



# So why go to SMART Tier 3 and sample?

- The EPA and the Natural Resource Trustees need to be concerned with the oil spill impacts which are not caused by the “coating effect” of the oil itself.
- During the turbulence of many spills, including mixing from wind and wave action, oil can be dispersed mechanically, and soluble components of oil can partition into the water column.
- The EPA and the Natural Resource Trustees need to be concerned with the oil spill impacts which are not caused by the “coating effect” of the oil itself.
- This involves chemical analysis, which triggers the need for SMART Tier 3.

- The Canadians and EPA's ORD have taught us that the lighter and more soluble oil components are more easily dispersed chemically. These are also the more toxic and biodegradable components, thus these are the most likely to cause environmental impact. In a localized or confined area, concentrations could build up and either toxicity, oxygen deficiency, or both could exert undesirable effects.
- Biodegradation potential of the suspended and dispersed residual oil and dispersant is also related to the chemical components, rather than on the broad categories of petroleum hydrocarbons or fluorescible organics.

- The NOAA SQuIRTs anticipate these problems and provide parameters and analytical method citations to address them. Many of the chemicals listed do not relate to oil spills, but some refer to the volatile and semivolatile components of crude and refined products.

- Since different oils have different relative concentrations of these fractions, assessing the environmental risk from the dispersible fraction requires that we either know what is in the originally-spilled oil or measure the byproducts in solution or suspension. The Environment Canada Catalog of Oil Properties can help predict this fraction.

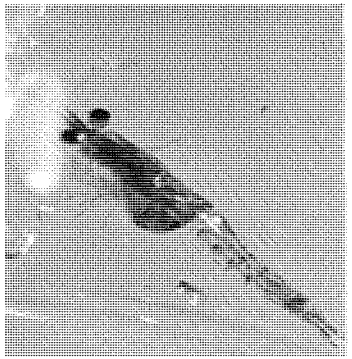
- National Academy of Sciences' 1972 Blue Book is still useful for water quality criteria relative to oil spills.

# SQuiRTs are for NOAA Hazmat screening-level use, but…

- Screening levels are based on EPA's Water Quality Criteria for acute exposure (highest 1 hour average, not to exceed once every 3 years). (This is effectively a grab sample.)
- For Semivolatile PAH, the concentration ranges between 7.7 and 3,980 ppb (ug/L)
- For Volatile Aromatics (BTEX) ranges between 530 to32,000 ppb.
- For Total Petroleum Hydrocarbons, there is no SQuiRT listed, but EPA's Method 8015B (GC/FID) is specified.
- SQuiRTs, are available on NOAA's website:

http://response.restoration.noaa.gov

## Results of 48 hour acute toxicity tests of 8 dispersants to the Gulf of Mexico invertebrate, mysid shrimp (*Americamysis bahia*)

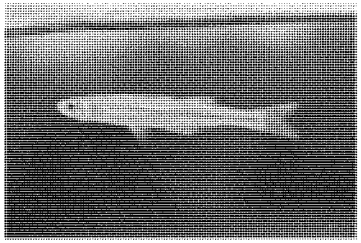


| Dispersant | This Study LC50 (ppm) [95% CI] | Toxicity Category | NCP Product Schedule LC50 (ppm) [95% CI] |
|---|---|---|---|
| Dispersit SPC 1000 | 12 [10-14] | Slightly Toxic | 16.6 [14.1-19.6] |
| Nokomis 3-AA | 30 [27-34] | Slightly Toxic | 20.2 [17.4-22.8] |
| **Corexit 9500A** | **42 [38-47]** | **Slightly Toxic** | **32.2 [26.5-39.2]** |
| Nokomis 3-F4 | 42 [38-47] | Slightly Toxic | 32.2 [28.4-36.5] |
| ZI -400 | 55 [50-61] | Slightly Toxic | 21.0 [17.9-24.5] |
| Sea Brat #4 | 65 [57-74] | Slightly Toxic | 14.0 [±10.4] |
| Saf-Ron Gold | 118 [104-133] | Practically Non-Toxic | 63.0* [52.9-75.1] |
| JD-2000 | 788 [627-946] | Practically Non-Toxic | 90.5* [76.1-108] |

* Classified as slightly toxic according to values provided in NCP Product Schedule

http://www.epa.gov/bpspill/dispersants-testing.html

## Results of 96 hour acute toxicity tests of 8 dispersants to the Gulf of Mexico fish, inland silverside (*Menidia beryllina)*



| Dispersant | This Study LC50 (ppm) [95% CI] | Toxicity Category | NCP Product Schedule LC50 (ppm) [95% CI] |
|---|---|---|---|
| Dispersit SPC 1000 | 2.9 [2.5-3.2] | Moderately Toxic | 3.5 [3.1-4.0] |
| Nokomis 3-F4 | 19 [16-21] | Slightly Toxic | 29.8 [24.0-35.4] |
| Nokomis 3-AA | 19 [17-21] | Slightly Toxic | 34.2 [29.2-37.95] |
| ZI -400 | 21 [18-23] | Slightly Toxic | 31.8 [28.7-35.1] |
| Saf-Ron Gold | 44 [41-47] | Slightly Toxic | 29.4 [25.2-34.3] |
| Sea Brat #4 | 55 [49-62] | Slightly Toxic | 30.0 [±16.2] |
| **Corexit 9500A** | **130 [122-138]** | **Practically Non-Toxic** | **25.2* [13.6-46.6]** |
| JD-2000 | >5,600 | Practically Non-Toxic | 407 [330-501] |

* Classified as slightly toxic according to values provided in NCP Product Schedule

http://www.epa.gov/bpspill/dispersants-testing.html

# SMARTer

- It is important to remember that in the rapidly changing conditions of spill response, flexibility and adaptability are essential for success. The sampling plan is dictated by many factors, including the availability of equipment and personnel, on-scene conditions, and the window of opportunity for dispersant application.
- The need for flexibility in sampling design, effort, and rapid deployment may dictate the nature and extent of the monitoring.
- To assist the monitoring efforts, it is important that the Unified Command agrees on the goals and objectives of monitoring and chooses the appropriate level of effort for the response.

# SMART Sampling and Analysis for Dispersant Application – A Final Message from the Old Timers

- Ken Biglane, the architect of the NCP and ERT, once said “I trust the oil I can see more than the oil I can't see.”
- Dr. Joseph P. Lafornara, 12/10/2003, quoted Ken and remarked on the Need for a National Dispersant Use Policy.
- The BP Deepwater Horizon Response showed that this policy is still needed.
- SMART performance data will be needed to craft a rational policy.

# Contact Information

- Allen.Harry@epa.gov
- www.epaosc.org/SMARTOSC/
- 732-321-6740 (ERT Main Number)
- 732-321-6660 (ERT Hotline)

**To:** Principe, Vanessa[Principe.Vanessa@epa.gov]
**From:** Wilson, Gregory
**Sent:** Thur 4/2/2015 3:52:29 PM
**Subject:** FW: Request for Proposal No. E15PS00027 (Broad Agency Announcement)
Conmy-EPA Letter T7-3.pdf
RFP E15PS00027 - Oil Spill Response Research.PDF

**From:** Conmy, Robyn
**Sent:** Monday, March 30, 2015 8:55 PM
**To:** Schubauer-Berigan, Joseph; Gilliland, Alice; Wilson, Gregory
**Subject:** FW: Request for Proposal No. E15PS00027 (Broad Agency Announcement)

FYI. EPA has been asked to submit a full proposal to DOI BSEE for conducting oil dispersion efficiency experiments in hypersaline (brine) waters. This supports knowledge gaps in preparing for Arctic oil spills. I will brief you on the timelines and full proposal when I return to the office next week.

Robyn

<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>/<>

Robyn N. Conmy, Ph.D.

Research Ecologist

USEPA/NRMRL/LRPCD

26 West MLK Drive

Cincinnati, Ohio 45268

513-569-7090 (office)

727-692-5333 (mobile)

conmy.robyn@epa.gov

**From:** Laikin-Credno, Caroline [mailto:caroline.laikin-credno@bsee.gov]
**Sent:** Monday, March 30, 2015 7:04 PM
**To:** Conmy, Robyn
**Subject:** Request for Proposal No. E15PS00027 (Broad Agency Announcement)

The Bureau of Safety and Environmental Enforcement (BSEE) has completed its review of the White Papers submitted under the Broad Agency Announcement No. E1EPS00027 for Proposed Research on Oil Spill Response Operations on the U.S. Outer Continental Shelf.

BSEE has determined that your White Paper has merit. Therefore, we would like your organization to submit a full proposal. A formal letter and a request for proposal are attached.

PLEASE REPLY BACK TO ME ACKNOWLEDGING RECEIPT OF THE RFP.

Thanks,

Caroline Laikin

BSEE Contracting Officer

**To:** Principe, Vanessa[Principe.Vanessa@epa.gov]
**From:** Wilson, Gregory
**Sent:** Wed 7/29/2015 8:07:28 PM
**Subject:** RT Plan
ICCOPR RT Plan Draft for Members 23JULY2015 v1 line nmbr_GW.docx

**MEMORANDUM**

**SUBJECT:** National Oil and Hazardous Substances Pollution Contingency Plan; Proposed Rule (Tier 2; RIN 2050- AE87) - **ACTION MEMORANDUM**

**FROM:** Mathy Stanislaus
Assistant Administrator

**THRU:** OEX (1105A)

**TO:** Lisa P. Jackson
Administrator (1102A)

**DEADLINE**

There is no court-ordered or statutory deadline associated with this action.

**PURPOSE**

The purpose of this Action Memorandum is to request your approval and signature of a proposed rule to amend the National Oil and Hazardous Substances Pollution Contingency Plan (NCP). The proposal specifically addresses the requirements in Subpart J of the NCP that govern the listing and use of dispersants, other chemicals, and other oil spill mitigating devices and substances for responses to oil spills in waters of the U.S.

**OVERVIEW**

In 1994, EPA revised the NCP in response to the passage of the Oil Pollution Act of 1990. The final rule established the current Subpart J regulatory requirements with respect to authorization of use, data requirements, dispersant effectiveness and toxicity testing protocols, surface washing agent testing protocol, bioremediation agent testing protocols, and requirements for adding products to the NCP Product Schedule (Schedule).

In April 2010, the Deepwater Horizon underwater oil well blowout released significant quantities oil into the Gulf of Mexico (Gulf). Dispersants were deployed over several miles of the Gulf both applied on surface slicks and directly injected into the oil gushing from the well riser, totaling close to two million gallons of dispersants. This unprecedented use of dispersants raised many questions about efficacy, toxicity, environmental trade-offs and monitoring challenges that EPA now seeks to address through these proposed revisions to Subpart J.

This action proposes to amend Subpart J requirements for the use of dispersants, and other chemical and biological agents to respond to oil spills in waters of the U.S., and considers concerns that arose during the Deepwater Horizon response regarding toxicity, efficacy, long-term environmental impacts, endangered species protection, and human health. Additionally, revisions to area planning requirements for dispersant use authorization and to toxicity and efficacy testing methodologies and listing thresholds, as well as advanced monitoring techniques are proposed. The revisions are a major component of EPA's effort to inform the use of dispersants and other chemical or biological agents to respond to oil discharges, using the federal government's experiences in the Gulf.

The proposed amendments would help to ensure that only products that perform effectively in laboratory testing would be listed on the Schedule for use in mitigating the effects of oil discharges in the environment. Submitters would be required to provide more detailed product application materials and human health and safety information, including instructions on how the product should be used in the field. The additional product information would aid On-Scene Coordinators (OSCs) and RRTs when evaluating specific product information and when deciding whether to use these products to mitigate hazards to the environment and human health caused by oil discharges. Prohibitions on using products in certain areas under certain conditions determined by OSCs, RRTs, and EPA would help ensure that responders are better able to prevent spilled oil from reaching navigable waters and other areas of concern, and to mitigate environmental effects when discharges occur.

Specifically, this action proposes to amend:

- *Definitions.* Revise definitions for Bioremediation agents, Burning agents, Chemical agents, Dispersants, Sinking agents, Sorbents, and Surface washing agents; new definitions for Bioaccumulation, Bioconcentration, Biodegradation, Biological agents, Herding agents, Products, and Solidifiers; and remove the definitions for Miscellaneous Oil Spill Control Agent (MOSCA) and Surface collecting agents.
- *General Requirements.* Revise to reflect new and amended regulatory definitions.
- *Authorization of Use.* Revise to clarify planning and preauthorization responsibilities, establish limitations and prohibitions on the use of certain agents, establish requirements for storage and use of agents, clarify authorities for requiring supplemental testing and information on agents, establish requirements for agent recovery from the environment, and provide notification of agent use.
- *Monitoring Requirements for Agent Use.* New monitoring requirements for major and/or continuous discharges.
- *General Product Information for Schedule Listing.* Revise and add new requirements, including designation of and testing for all product categories under which the listing is requested, Material Safety Data Sheets, sample product labels, shelf life, collection and recovery, persistence in the environment, storage and use conditions, physical and chemical properties, component identities, concentration limits on National Water Quality Standards and Criteria contaminants, laboratory accreditations, submission of all testing data and calculations, production capabilities, and any other data or certification informing the product's performance capabilities or environmental benefits.
- *Dispersant Testing and Listing Requirements.* New efficacy testing methodology using a baffled-flask test, new developmental and sub-chronic toxicity testing requirements, revisions to acute toxicity testing methodologies, revisions to the listing criteria, and new use limitations to saltwater environments.
- *Surface Washing Agent Testing and Listing Requirements.* Revise the acute toxicity testing methodology and listing requirements, new efficacy testing requirements and listing criteria, and new use limitations based on product testing for salt and/or freshwater environments.
- *Bioremediation Testing and Listing Requirements.* Revise the efficacy and acute

toxicity testing methodologies and listing criteria, new exceptions for specified products, and new use limitations based on product testing for salt and/or freshwater environments.

- *Solidifier Testing and Listing Requirements.* Revise the acute toxicity testing methodology and listing criteria, and new use limitations based on product testing for salt and/or freshwater environments.
- *Herding Agent Testing and Listing Requirements.* Revise the acute toxicity testing methodology and listing criteria, and new use limitations based on product testing for salt and/or freshwater environments.
- *Sorbent Testing and Listing Requirements.* Publicly available list of known, non-proprietary sorbents to be made available in lieu of listing sorbents on the Schedule; requirements for data, information and certifications for sorbent products with components other than those specifically identified as non-proprietary.
- *Submissions of Confidential Business Information.* Revise the allowable confidential business information claims and reporting procedures.
- *Addition of a Product to the Schedule.* Revise submission requirements, including the package contents, EPA's review, request for review of decision, changes to a listed product, and transitioning of listed products from the current Schedule to the new Schedule.
- *Mandatory Product Disclaimer.* Revise the product disclaimer requirements.
- *Removal of a Product from the Schedule.* Revise basis for removal and appeals process.
- *Appendix E to Part 300 – Oil Spill Response.* Remove this appendix to the NCP.

**IMPACTS**

We estimate the total cost for this action ranges from approximately $360,000 to $504,000 annually (2012$). This proposed action is aimed at ensuring that chemical and biological agents have met rigorous efficacy and toxicity requirements, that product submitters provide important use and safety information, and that the planning and response community is equipped with the proper information to authorize and use the products in a judicious and effective manner.

Under the terms of Executive Order 12866, this final action is a "significant regulatory action" because it raises novel legal or policy issues arising out of legal mandates, the President's priorities, or the principles set forth in the Executive Order. Therefore, this action was submitted to OMB for review and the Agency has prepared a regulatory analysis to support it.

After considering the economic impacts of this action on small entities, the Agency certifies that this action would not have a significant economic impact on a substantial number of small entities. This rule contains no regulatory requirements that might significantly or uniquely affect small governments. Finally, this rule does not have federalism implications.

**STAKEHOLDER INVOLVEMENT**

Numerous groups of stakeholders have provided input for EPA's consideration,

representing sectors that include: agent manufacturers, testing laboratories, research and development companies (R&D), oil production industry, farming and fisheries industry, tourism industry, and emergency responders subject to the Schedule section of the NCP regulations. EPA has also sought input from key federal partners, including DOI/BSEE, DOC/NOAA and DHS/USCG. This proposed action reflects their concerns.

**INTERNAL REVIEW**

A workgroup comprised of OPEI, OGC, OECA, ORD, OW, OCSPP, and Regions 1, 2, 3, 5, 6, 8 and 9 has been established for the Subpart J of the NCP rulemaking effort. All of the offices and Regions represented in the workgroup concurred with the action submitted for OMB review, and comments made by workgroup members during Final Agency Review were addressed.

**PEER REVIEW**

Several supporting technical documents were submitted for peer review. One technical product supporting this action, the dispersant effectiveness test protocol, was subjected to peer review procedures as defined by the Agency's Peer Review Handbook through its publication in two peer-reviewed journal articles. The bioremediation efficacy test protocol was also subject to peer review procedures via publication in a single peer-reviewed journal article. The other technical requirements are based on standard methodologies.

**PLAIN LANGUAGE**

This final action was written in a clear and concise manner, and was organized to serve the reader's needs.

**OMB TRANSACTIONS**

EPA submitted this action to the Office of Management and Budget (OMB) for review under EO 12866 because it raises novel legal or policy issues arising out of legal mandates, the President's priorities, or the principles set forth in the Executive Order. The action was cleared by OMB on November XX, 2012. The interagency review included the Departments Commerce, Interior, and Homeland Security. All OMB recommendations and interagency comments have been addressed.

**ANTICIPATED EXTERNAL REACTION**

The Agency expects high interest and a mixed response to this action.

State and local officials are expected to favor the proposal given that it would provide additional testing and information to assist them when determining the appropriateness of chemical and biological agent use in response to an oil discharge. Tribal governments are expected to have limited interest.

Product submitters may have concerns regarding the added testing costs and the timetable to retest existing products on the Schedule. Submitters representing small product manufacturers may ask for some relief from retesting their products for efficacy and/or toxicity. Both the oil and the emergency response industries may express concerns regarding the new monitoring requirements targeted at the responsible party who plans to use dispersants in response to

potential discharges that are major or of national significance. Both the agricultural and tourism stakeholders are expected to favor the proposal as it enhances the safeguards in place when using agents that may directly affect their source of revenue.

Environmental groups are generally expected to support this action, as it offers amendments that better consider agent toxicity, efficacy, long- term environmental impacts, endangered species protection, and human health concerns, and the tradeoffs of using these agents to mitigate the harmful environmental effect of oil discharges. The use of dispersants has attracted major attention from non-governmental organizations and stakeholders in the U.S. since their use and benefit is site and spill specific. Area plans that include preauthorization of dispersants have caused some concern with NGOs, state officials, wildlife (including fish) protection organizations, and recreational and industrial fishing interest.

Congressional interest is expected, particularly from those representing constituencies that could be visibly affected by an oil discharge, and those affected by the listing, planning and response provisions. Congressional members have also expressed constituent concerns about the lack of use their products and may have and interest in the proposed transition to the new Schedule.

Media and national press interest is expected, particularly as they report on the progress, long-term environmental effects and recovery of the areas affected directly by the recent Deepwater Horizon event. There has been some positive coverage of the Subpart J regulatory program and the use of products in the trade and emergency response press. We expect these publications to carry stories summarizing the contents of the rule for their readers.

**STAFF CONTACTS**

The contacts for this action are XXXXX.

**RECOMMENDATION**

I recommend that you approve and sign this proposed action amending the NCP rule.

**To:** Mandsager, Kathy[kathy.mandsager@unh.edu]; Conmy, Robyn[Conmy.Robyn@epa.gov]; 'fingasmerv@shaw.ca'[fingasmerv@shaw.ca]; 'tchazen@utk.edu'[tchazen@utk.edu]; 'Robert Jones - NOAA Federal'[robert.jones@noaa.gov]; 'Samantha Joye'[mandyjoye@gmail.com]; 'ken.lee@csiro.au'[ken.lee@csiro.au]; 'mbleigh@alaska.edu'[mbleigh@alaska.edu]; 'karl.linden@colorado.edu'[karl.linden@colorado.edu]; 'kmmcfarlin@alaska.edu'[kmmcfarlin@alaska.edu]; msmiles@lsu.edu[msmiles@lsu.edu]; 'thomas.s.coolbaugh@exxonmobil.com'[thomas.s.coolbaugh@exxonmobil.com]; 'Mathijs.Smit@shell.com'[Mathijs.Smit@shell.com]; Sprenger, Mark[Sprenger.Mark@epa.gov]
**Cc:** Lindsey R Howard[lrw23@wildcats.unh.edu]; nancy.kinner@unh.edu[nancy.kinner@unh.edu]; Kinner, Peter[Peter.Kinner@unh.edu]; Wilson, Gregory[Wilson.Gregory@epa.gov]; Principe, Vanessa[Principe.Vanessa@epa.gov]; 'tracee.nguyen@csiro.au'[tracee.nguyen@csiro.au]; 'Ian Gaudreau'[ipu3@unh.edu]; 'doug.helton@noaa.gov'[doug.helton@noaa.gov]; 'Gary Shigenaka - NOAA Federal'[gary.shigenaka@noaa.gov]
**From:** Ian P Gaudreau
**Sent:** Tue 3/31/2015 11:11:22 PM
**Subject:** Re: Degradation & Fate update - NEXT DISCUSSION - 3/31 at 11 ET
Brakstad et al 2015.pdf
Mervis 2014.pdf

Hello everyone,

From today's discussion, two papers have been added to the group of papers we have been working with recently (they are also attached in this email):

Mervis 2014 (bias toward not publishing null hypothesis results)

Brakstad et al 2015 (biodegradation at low temperatures and different droplet sizes)

Ian Gaudreau

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**From:** Mandsager, Kathy <kathy.mandsager@unh.edu>
**Sent:** Tuesday, March 31, 2015 12:24 PM
**To:** 'Conmy, Robyn'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu'; 'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; 'Mathijs.Smit@shell.com'; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** Lindsey R Howard; Kinner, Nancy; Kinner, Peter; 'wilson.gregory@epa.gov'; 'principe.vanessa@epa.gov'; 'tracee.nguyen@csiro.au'; 'Ian Gaudreau'; 'doug.helton@noaa.gov'; 'Gary Shigenaka - NOAA Federal'
**Subject:** RE: Degradation & Fate update - NEXT DISCUSSION - 3/31 at 11 ET

Attached is the paper in pdf format.

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**From:** Mandsager, Kathy
**Sent:** Tuesday, March 31, 2015 11:14 AM
**To:** 'Conmy, Robyn'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu'; 'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; 'Mathijs.Smit@shell.com'; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** 'Lindsey R Howard'; Kinner, Nancy; Kinner, Peter; 'wilson.gregory@epa.gov'; 'principe.vanessa@epa.gov'; 'tracee.nguyen@csiro.au'; 'Ian Gaudreau'; 'doug.helton@noaa.gov'; 'Gary Shigenaka - NOAA Federal'
**Subject:** RE: Degradation & Fate update - NEXT DISCUSSION - 3/31 at 11 ET

Additional paper for review. http://ac.els-cdn.com/S0025326X15000855/1-s2.0-S0025326X15000855-main.pdf?_tid=a972873c-d7b7-11e4-9464-00000aab0f27&acdnat=1427814635_2731a355cf42e8b64679699bc221613

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**From:** Mandsager, Kathy
**Sent:** Monday, March 30, 2015 4:43 PM
**To:** 'Conmy, Robyn'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu'; 'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; 'Mathijs.Smit@shell.com'; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** 'Lindsey R Howard'; Kinner, Nancy; Kinner, Peter; 'wilson.gregory@epa.gov'; 'principe.vanessa@epa.gov'; 'tracee.nguyen@csiro.au'; 'Ian Gaudreau'; 'doug.helton@noaa.gov'; 'Gary Shigenaka - NOAA Federal'; Mandsager, Kathy
**Subject:** RE: Degradation & Fate update - NEXT DISCUSSION - 3/31 at 11 ET

This is a reminder of our WebEx meeting tomorrow.

**From:** Mandsager, Kathy
**Sent:** Friday, March 20, 2015 6:19 PM
**To:** 'Conmy, Robyn'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu'; 'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; 'Mathijs.Smit@shell.com'; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** 'Lindsey R Howard'; Kinner, Nancy; Kinner, Peter; 'wilson.gregory@epa.gov'; 'principe.vanessa@epa.gov'; 'tracee.nguyen@csiro.au'; 'Ian Gaudreau'; 'doug.helton@noaa.gov'; 'Gary Shigenaka - NOAA Federal'
**Subject:** RE: Degradation & Fate update - NEXT DISCUSSION - 3/31 at 11 ET

Mark your calendar! This is to confirm our next meeting for **Tuesday, March 31** beginning at 11:00 am ET.

Her are the WebEx directions to join this meeting. Thank you!

**Degradation & Fate Group**
Tuesday, March 31, 2015
11:00 am | Eastern Daylight Time (New York, GMT-04:00) | 2 hrs

Join WebEx meeting

Meeting number: 734 916 289

**Join by phone**
**1-855-244-8681** Call-in toll-free number (US/Canada)
**1-650-479-3207** Call-in toll number (US/Canada)
Access code: 734 916 289
Global call-in numbers | Toll-free calling restrictions

Can't join the meeting? Contact support.

**From:** Mandsager, Kathy
**Sent:** Thursday, March 19, 2015 8:31 AM
**To:** 'Conmy, Robyn'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu';

'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; 'Mathijs.Smit@shell.com'; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** 'Lindsey R Howard'; Kinner, Nancy; Kinner, Peter; 'wilson.gregory@epa.gov'; 'principe.vanessa@epa.gov'; 'tracee.nguyen@csiro.au'; 'Ian Gaudreau'; 'doug.helton@noaa.gov'; 'Gary Shigenaka - NOAA Federal'
**Subject:** RE: Degradation & Fate update - NEXT DISCUSSION

I greatly appreciate your patience with this process. Please **cancel** the tentative hold on your calendar for tomorrow 3/20. Since we would greatly appreciate a majority of this group to participate in this 2-hour WebEx meeting, I am making another attempt at scheduling this call. Please use this doodle poll (all times noted are ET). Thank you to each of you!

Doodle poll here>> http://doodle.com/2w3gyb3gv4sv7iek

**From:** Mandsager, Kathy
**Sent:** Monday, March 16, 2015 4:39 PM
**To:** 'Conmy, Robyn'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu'; 'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; 'Mathijs.Smit@shell.com'; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** 'Lindsey R Howard'; Kinner, Nancy; Kinner, Peter; 'wilson.gregory@epa.gov'; 'principe.vanessa@epa.gov'; 'tracee.nguyen@csiro.au'; 'Ian Gaudreau'
**Subject:** RE: Degradation & Fate update - NEXT DISCUSSION

In the spirit of trying to keep everyone informed – there will NOT be a meeting tomorrow at 2 (see request below). I was unable to gain a quorum. Please continue to hold this Friday 3/20 as a potential meeting time. And if you have not yet responded with your availability, please let me know if you could possibly make in on **3/20 beginning at 1pm ET.**

Thank you.

**From:** Mandsager, Kathy
**Sent:** Monday, March 16, 2015 9:38 AM
**To:** 'Ian P Gaudreau'; 'Conmy, Robyn'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu'; 'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; 'Mathijs.Smit@shell.com'; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** 'Lindsey R Howard'; Kinner, Nancy; Kinner, Peter; 'wilson.gregory@epa.gov'; 'principe.vanessa@epa.gov'; 'tracee.nguyen@csiro.au'; 'Ian Gaudreau'
**Subject:** RE: Degradation & Fate update - NEXT DISCUSSION
**Importance:** High

While these papers are fresh on your mind, I am offering some dates as soon as possible for our next meeting. Kindly let me know if you can make yourself available for about a 2-hour timeslot at any of the following times:

Tuesday (tomorrow) 3/17 beginning at 2:00 pm ET

Friday 3/20 beginning at 12noon ET

Friday 3/20 beginning at 1:00 pm ET

Friday 3/20 beginning at 2:00 pm ET

Friday 3/20 beginning at 3:00 pm ET

Thursday 3/26 at 10:00 am ET

Monday 3/30 beginning at 2:20 pm ET

A speedy reply will be greatly appreciated. Thank you!

**From:** Ian P Gaudreau [mailto:ipu3@wildcats.unh.edu]
**Sent:** Friday, March 13, 2015 10:16 AM
**To:** 'Conmy, Robyn'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu'; 'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; 'Mathijs.Smit@shell.com'; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** Lindsey R Howard; Mandsager, Kathy; Kinner, Nancy; Kinner, Peter; 'wilson.gregory@epa.gov'; 'principe.vanessa@epa.gov'; tracee.nguyen@csiro.au; Ian Gaudreau
**Subject:** Degradation & Fate update - Official Papers

Hi folks,

Thank you for hanging in there on the conference call Wednesday. We really

appreciate all of the hard work you have been doing. The 13 official papers you decided you would review and use as the basis for your comments (e.g. knowns, uncertainties) on the effect of chemical dispersants on oil biodegradation are:

- Venosa & Holder 2007
- Prince et al. 2013
- Prince & Butler 2014
- Mcnaughton et al. 2003
- McFarlin et al. 2014
- Mason et al. 2012
- Lindstrom & Braddock 2002
- Kleindienst et al. 2015
- Chakroborty et al. 2012
- Campo et al. 2013
- Bruheim et al. 1997
- Bruheum et al. 1999
- Baelum et al. 2012

These papers are all located in a folder on BOX entitled "Papers selected by panel - Effect of Chemical Dispersants on Oil Biodegradation". This link can be found here: https://unh.app.box.com/files/0/f/3252405678/Papers_selected_by_panel_-_Effect_of_Chemical_Dispersants_on_Oil_Biodegradation

Kathy will be contacting you to schedule what will hopefully be our final meeting of the Degradation & Fate group.

In preparation for the meeting, please re-read the paper and if you have time, send Kathy the conclusions that you derive from these references regarding what is known

and uncertain about the effect of chemical dispersants on the biodegradation of oil, particularly as it applies to the Arctic.

Also, we need your feedback on a paper by Harris et al. 2002 (paper is attached in this email). Would you like us to add this paper to the "Papers selected by panel - Effect of Chemical Dispersants on Oil Biodegradation" folder on BOX? Here is the citation:

Harris, B.C. et al. 2002. Nutrient effects on the biodegradation rates of chemically-dispersed crude oil. *In* Twenty-Fifth Arctic and Marine Oilspill Program (AMOP) Technical Seminar, Nineteenth Technical Seminar on Chemical Spills (TSOCS) and Fourth Biotechnology Solutions for Spills (BIOSS): June 11 to 13, 2002, Westin Calgary Hotel, Calgary, Alberta, Canada: Proceedings. Ottawa, Ont.: Environment Canada. pp. 877-893.

Thanks again for your time and energy. I look forward to talking with you again.

**Nancy E. Kinner, Ph.D.**

**University Professor**

**Professor Civil/Environmental Engineering**

**UNH Director, Coastal Response Research Center**

**Director, Center for Spills in the Environment**

**236 Gregg Hall**

**University of New Hampshire**

**Durham, NH 03824**

**Phone: 603-862-1422**

**Fax: 603-862-3957**

**http://www.crrc.unh.edu**

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# Biodegradation of dispersed Macondo oil in seawater at low temperature and different oil droplet sizes

Odd G. Brakstad ⇑, Trond Nordtug, Mimmi Throne-Holst

SINTEF Materials and Chemistry, Environmental Technology, Dept. Applied Environmental Biology and Chemistry, N-7465 Trondheim, Norway

article info

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Available online xxxx

Keywords:
Oil
Biodegradation
Dispersions
Seawater
Low temperature
Droplet size

abstract

During the Deepwater Horizon (DWH) accident in 2010 a dispersant (Corexit 9500) was applied at the wellhead to disperse the Macondo oil and reduce the formation of surface slicks. A subsurface plume of small oil droplets was generated near the leaking well at 900–1300 m depth. A novel laboratory system was established to investigate biodegradation of small droplet oil dispersions (10 lm or 30 lm droplet sizes) of the Macondo oil premixed with Corexit 9500, using coastal Norwegian seawater at a temperature similar to the DWH plume (4–5 ffC). Biotransformation of volatile and semivolatile hydrocarbons and oil compound groups was generally faster in the 10 lm than in the 30 lm dispersions, showing the importance of oil droplet size for biodegradation. These data therefore indicated that dispersant treatment to reduce the oil droplet size may increase the biodegradation rates of oil compounds in the deepwater oil droplets.

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## 1. Introduction

During the Deepwater Horizon (DWH) incident some of the oil was dispersed as small droplets in the deep ocean at depths of 900–1300 m near the leaking well, and at water temperatures of 4–6 ffC (Camilli et al., 2010; Reddy et al., 2012). Simulations of the plume trajectories predicted that oil droplets with diameters between 10 and 50 lm would form in a distinct subsurface layer and be transported horizontally, while droplets larger than 90 lm rapidly rose to the surface (North et al., 2011). Samples from the deepwater plume showed enrichment of water-soluble components (Camilli et al., 2010). Measurements of PAH in water samples during the release showed rapid decrease with distance from the release point. The responders began injecting the chemical dispersant Corexit 9500A at the wellhead in early May 2010 to reduce the amount of oil that formed surface slicks and reached the Gulf of Mexico (GoM) coastlines (Atlas and Hazen, 2011; Kujawinski et al., 2011). In addition, surface operations included mechanical recovery techniques and application of the chemical dispersants Corexit 9527 and 9500A (Coastal Response Research Center, 2010).

It was early observed that the deepwater plume stimulated bacteria associated with hydrocarbon biodegradation in cold seawater (Oceanospirillaceae, Pseudomonas, Cycloclasticus, Colwellia, Pseudoalteromonas, Methylophaga) (Valentine et al., 2010; Hazen et al., 2010; Redmond and Valentine, 2012; Dubinsky et al., 2013), and data from the field and from laboratory experiments indicated short biodegradation half-lives for $nC_{13}$–$nC_{26}$ alkanes, ranging from 1 to 8 days (Hazen et al., 2010). A sequential and pulsed propagation of bacteria degrading specific hydrocarbons was suggested, including n-alkanes, aromatics and $C_1$–$C_3$ gas components (Valentine et al., 2012; Dubinsky et al., 2013). Results from stable isotope analyses reported that close to 70% of the oxygen consumption in the deepwater plume was related to bacterial respiration of propane and ethane (Valentine et al., 2010), while methane oxidation was delayed (Valentine et al., 2010; Kessler et al., 2011).

Biodegradation rates of components in dispersed oil are normally expected to increase when oil droplet size is reduced, for instance by treatment of the oil with chemical dispersants. Smaller droplets will generate larger oil–water interphase areas for the oil-degrading bacteria to attach to, and dissolution of water-soluble compounds will increase. Volatile oil compounds will rapidly dissolve during subsurface spills and thereby become subject to biodegradation. In contrast volatiles will largely evaporate after surface spills. Several laboratory studies have shown that dispersant treatment of dispersible oils increase oil compound biodegradation (Siron et al., 1995; Venosa and Holder, 2007; Prince et al., 2013; McFarlin et al., 2014; Brakstad et al., 2014).

To our knowledge, no laboratory studies have attempted to relate the biodegradation of oil compounds to measured droplet sizes in the dispersions. We therefore established a novel

⇑ Corresponding author. Tel.: +47 98243447; fax: +47 73597043.
E-mail address: odd.brakstad@sintef.no (O.G. Brakstad).

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experimental system for comparing oil dispersions of different small droplet sizes in natural seawater. This system was based on combining an oil dispersion generator (Nordtug et al., 2011) and a slowly rotating carousel system to generate small droplet dispersions and avoid droplets rising to the surface. The primary aim of our study was therefore to quantify biodegradation of hydrocarbons in dispersions with defined oil droplet sizes relevant for chemically dispersed oil, and at low seawater temperatures, corresponding to deepwater discharges. Biodegradation of chemically dispersed Macondo oil at two median oil droplet sizes (10 and 30 lm) in natural seawater at 4–5 ffC was investigated with this system. Norwegian coastal seawater was used in the study, but experimental conditions (oil, oil droplet size distributions and seawater temperature) were relevant to the DWH deepwater plume.

## 2. Materials and methods

### 2.1. Oil, dispersant and seawater used in experiments

Unweathered Macondo (MASS) oil was collected from a riser pipe connected to the well on 22 May 2010. COREXIT 9500A (Nalco, Sugar Land, TX) dispersant was used at a dispersant-to-oil ratio (DOR) of 1:100. Seawater was collected from a depth of 80 m (below thermocline) in a Norwegian fjord (Trondheimsfjord; 63ff26°N, 10ff23°E), outside the harbor area of Trondheim, the water is supplied via a pipeline system to our laboratories. The water source is considered to be non-polluted and not influenced by seasonal variations. The salinity of the seawater was 34‰, with a water temperature of 6–8 ffC and dissolved oxygen (DO) of approximately 8 mg/L when reaching our laboratory (Brakstad et al., 2004).

### 2.2. Oil dispersion generator and carousel system

An oil droplet generator was used for preparing oil dispersions with defined droplet size distributions, as previously described (Nordtug et al., 2011). The system consists of 3 chambers with an inner diameter of 8 mm connected by nozzles with a diameter of 0.5 mm. Oil dispersions with defined oil droplet size distributions and concentrations are generated by injecting oil via a capillary into a flow of seawater which moves through the chambers (Nordtug et al., 2011). Oil droplet concentrations and size distribution were determined by Coulter Counter analyses (see below). Flasks (2 L; Schott) were baked (450 ffC; 3 h) and soaked overnight (4% Deconex 11 Universal, Borer, Switzerland), washed with detergent (Neodisher N, Dr. Weigert, Germany), and thoroughly rinsed and autoclaved (121 ffC, 20 min) before use.

The flasks were completely filled with oil dispersions (no headspace or air bubbles) and mounted on a carousel system. During mounting of flasks and biodegradation experiments the wheels were slowly rotated around the carousel axis (0.75 r.p.m.) by a gear motor (SEW Eurodrive, Moss, Norway). In the main biodegradation experiment described here, four carousels with double sets of wheels, holding up to 16 flasks each, were used.

### 2.3. Biodegradation experiment

The MASS oil was heated at 50 ffC for 30 min, mixed by shaking for 3 min, and cooled to room temperature, after which it was mixed with the dispersant Corexit 9500A (DOR 1:100) at room temperature. This dispersant was shown to effectively disperse the Macondo oil (Daling et al., 2014). Pre-adaption of the seawater prior to the biodegradation experiments was conducted by diluting a stock dispersion (200 mg/L oil; oil droplet size 10 lm) to 0.2 mg/L Macondo oil (measured by Coulter Counter) in natural unfiltered seawater (pre-incubated over night at 5 ffC) in 2-L flasks completely filled (no air bubbles) with the dispersions, with incubation in the carousel system at 5 ffC for 5 days (rotation 0.75 r.p.m.). The experiment was then started by generating dispersions in the pre-adapted seawater with median oil droplet sizes of 10 lm or 30 lm and nominal oil concentration of 2 mg/L from a stock oil dispersion (200 mg/L oil) in natural unfiltered seawater. Dispersions of 10 lm or 30 lm median oil droplet sizes and 2 mg/L nominal concentrations were also prepared in sterile-filtered (0.2 lm) seawater (incubated at 4–5 ffC overnight before use) supplemented with $HgCl_2$ (100 mg/L), to minimize bacterial growth. Immediately after generation of dispersions flask were mounted on the carousel at slow rotation (0.75 r.p.m.). Flasks with experimental blank samples (unfiltered seawater without oil) were also included in the experiment for background analyses. Experiments were conducted at 5 ffC for up to 64 days. Flasks (triplicate samples; 2.3 L sample) of dispersions in natural seawater were sacrificed for analyses after 15 min on the carousel (0-day samples) and after 2, 4, 8, 16, 32, or 64 days of incubation on the carousels. One sterilized control flask and one experimental blank flask were also sacrificed for analyses at the each sampling point.

### 2.4. Analyses

#### 2.4.1. Oil droplet analyses

Oil droplet concentrations and size distributions were determined by Coulter Counter measure (Beckman Multisizer 4; Beckman Coulter Inc., Brea, CA, USA) fitted with either 100 lm or 280 lm apertures, for measurement of droplets within a diameter range of 2–60 lm or 5.6–100 lm, respectively. Filtered (0.22 lm) seawater was used as electrolyte. All median droplet sizes reported here are expressed as median droplets diameter on droplet volume if not otherwise mentioned.

#### 2.4.2. Chemical analyses

Samples of dispersions and seawater were solvent–solvent extracted with dichloromethane (DCM) for measurements of semivolatile organic compounds (SVOC) by gas chromatographic methods. The flask glass walls were also rinsed with DCM after removal of dispersions to extract material attached to the glass walls. All extracts were pooled before analyses. A gas chromatograph coupled to a flame ionization detector (GC-FID; Agilent 6890 N with 30 mDB1 column; Agilent Technologies) was used for quantification of extracted $C_{10}$–$C_{36}$ saturates separated according to boiling points, termed as total petroleum hydrocarbons extractable organic carbon (TEOC), while 96 individual targeted compounds ($C_{10}$–$C_{36}$ n-alkanes, decalines, phenols, 2- to 5-ring polyaromatic hydrocarbons (PAH) and 17a(H),21b(H)-Hopane (30ab Hopane) were analyzed in a gas chromatograph coupled to a mass spectrometer (GC–MS; Agilent 6890 plus GC coupled with an Agilent 5973 MSD detector, operated in Selected Ion Monitoring [SIM] modus; Agilent Technologies), as recently described (Brakstad et al., 2014). Dispersions were acidified (pH < 2) for analyses of 87 targeted volatile organic carbon (VOC) compounds in a Purge & Trap unit (Teledyne Tekmar Atomx; Mason OH, USA.) coupled to a GC–MS (Agilent 6890 N GC and an Agilent 5975B MSD detector; Agilent Technologies)(P&T GC–MS). The VOC and SVOC target compounds included in GC–MS analyses are shown in Table S1. The response values for individual target analytes were determined, with a signal-to-noise ratio of 10 as the lower detection limit, and a lower limit of detection (LOD) of 0.01 lg/L was defined for individual oil compounds.

#### 2.4.3. Temperature, dissolved oxygen, nutrients, and biomass

Air and seawater temperatures were logged through the experimental period. Dissolved oxygen was measured by a

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dissolved oxygen meter (YSI, Inc., Yellow Springs, OH). Nutrient analyses included $NO_3$–N + $NO_2$–N (ISO 13395), $NH_4$–N (ISO 11732), o-$PO_4$–P (ISO 15681-2), and total Phosphorous (ISO 15681-2), analyzed by Eurofins Environment Testing Norway, Bergen, Norway. Microbial biomass concentrations were determined by epifluorescence microcopy analyses of samples stained by the nucleic acid stain 4$^0$,6-diamidino-2-phenylindol (Porter and Feig, 1980).

### 2.5. Calculations and statistics

Non-linear regression analyses were performed by a 1st order rate approach with determination of lag-phases included using the option "plateau followed by one-phase decay" in GraphPad Prism vs. 6.0 (GraphPad Software Inc., La Jolla, CA, USA). Rate coefficients (k1) were determined for the decay-period, the plateau period defined the lag-phase, and half-lives were determined from rate coefficients and plateau periods (t1/2 = plateau period + 0.693/k1). Rate data were determined for both single oil components and for 22 oil compound groups described in the Oil-Spill Contingency and Response model OSCAR (Reed et al., 2000). The group composition is described in Table S1.

Column statistics were compared by Wilcoxon matched paired test in GraphPad Prism vs. 6.

## 3. Results and discussion

### 3.1. Generation and maintenance of oil dispersions over time

Dispersions of Macondo oil mixed with Corexit 9500A (DOR of 1:100) were generated by different seawater flow-rates through the oil droplet generator system, from 50 to 150 ml/min. This resulted in oil dispersions with median droplet size distributions of approximately 10 l m to 30 l m in diameter (Fig. 1). The oil pump of the dispersion generator was set to generate fixed nominal oil concentrations during the dispersion generation (0.2–200 mg oil per L of water), and good agreement between nominal oil concentrations and measured oil droplet concentrations was recorded (data not shown). Recent studies have shown that nearly the same oil droplet size distribution is generated in this system both with and without premixing of oil with chemical dispersant (Nordtug et al., 2011).

The carousel system was developed for maintaining the droplet size distribution in the oil dispersions while incubating the dispersions over time. All experiments in the carousels were conducted in air-tight flasks without headspace to avoid evaporative depletion. The system was able to handle dispersions of fresh Macondo oil with small droplets, in the diameter size range of 10–30 l m, with rising velocities of 1.6–14.4 cm/h, according to Stoke's law. We believe the ability of keeping the droplets in suspension is due to the combined effect of the turbulence created in the flasks and the fact that the oil droplet rising velocities will make them constantly change direction in relation to any fixed point at the flasks inner surface. Larger than 30 l m oil droplets resulted in inhomogeneous dispersions during transfer from dispersion generator to flasks in carousel system because of elevated rising velocities. In initial experiments with 10 l m median volumetric droplet dispersions in a sterilized system (filtered seawater poisoned with $HgCl_2$), the droplet sizes were maintained for at least 28 days in the carousel system, while measured droplet concentration decreased (see Supplementary Information, Fig. S1).

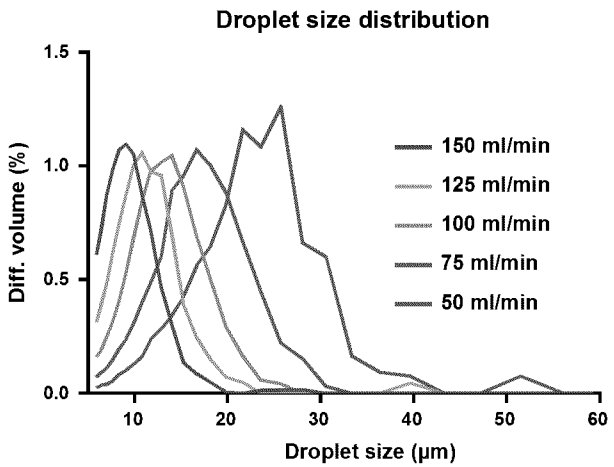


Fig. 1. Average oil droplet size distributions generated in the oil dispersion generator at different seawater flow-rates after premixing of the oil with Corexit 9500A.

### 3.2. Biodegradation experiment with two dispersions of different oil droplet size distributions

An oil dispersion biodegradation experiment was performed at 5 fC (64 days) with nominal oil concentrations of 2 mg/L generated in the dispersion generator at median oil droplet sizes on volume of 10 l m and 30 l m in diameter, and with natural seawater pre-adapted to the oil and temperature (see Section 2). The low oil concentration used in this experiment is consistent with recent recommendations to avoid too high oil loading during biodegradation studies of dispersed oil (Lee et al., 2013). Seawater pre-adaption was included since many offshore oil production areas may be exposed to hydrocarbons through natural seepage or produced water releases. For instance, a recent hydrocarbon seepage flux of 2.2–18 ┐ $10^7$ tons per year has been estimated for the GoM region, corresponding to 14–120% of the DWH discharge rate (Smith et al., 2014). Analyses of macronutrients ($NO_3$ + N $O_2$–N, $NH_4$–N and o-$PO_4$–P) and dissolved oxygen showed no apparent limitations in oxygen or inorganic nutrient levels during the biodegradation experiment (Supplementary Information, Figs. S2 and S3).

#### 3.2.1. Oil droplet sizes and concentrations

The oil droplet size distributions and concentrations were followed in the dispersions during the biodegradation experiment (Fig. 2). Results from Coulter Counter analyses showed that the initial median oil droplet size distributions in the 10 l m and 30 l m dispersions were 11.0 ± 0.04 l m and 29.4 ± 3.5 l m, and that the 10 l m and 30 l m dispersions represented oil surfaces of 10.9 ± 0.2 ┐ $10^5$ and 5.4 ± 0.9 ┐ $10^5$ l $m^2$/ml, respectively. The dispersions with the smaller droplets therefore contained approximately twice the surface area of the dispersions with the larger droplet. Assuming a microbial size of 1 l m in diameter and the maximum microbial density of 1 cell/l $m^2$ of oil droplet surface area (Horowitz et al., 1975; Vilcaez et al., 2013) the initial oil droplet concentrations represented sufficient surface areas for colonization of up 10 ┐ $10^5$ cells/ml in the 10 l m dispersions and 5 ┐ $10^5$ cells/ml in the 30 l m dispersions. Initial cell concentrations determined by epifluorescence microscopy were 8 ┐ $10^5$ and 12 ┐ $10^5$ cells/ml in the 10 l m and 30 l m dispersions, respectively. The oil droplets therefore represented surface areas for attachment of the entire bacterial population in the 10 l m dispersions and approximately 40% of the population in the 30 l m dispersions at the start of the experiment.

The oil droplet size distributions during the biodegradation period (Fig. 2A) were maintained in the 10 l m dispersions (average median droplet size of 3 replicates ranging from 10.7 to 13.4 l m in the natural unfiltered seawater and 8.5–11.1 l m in sterile dispersions). However, the 30 l m dispersions in natural

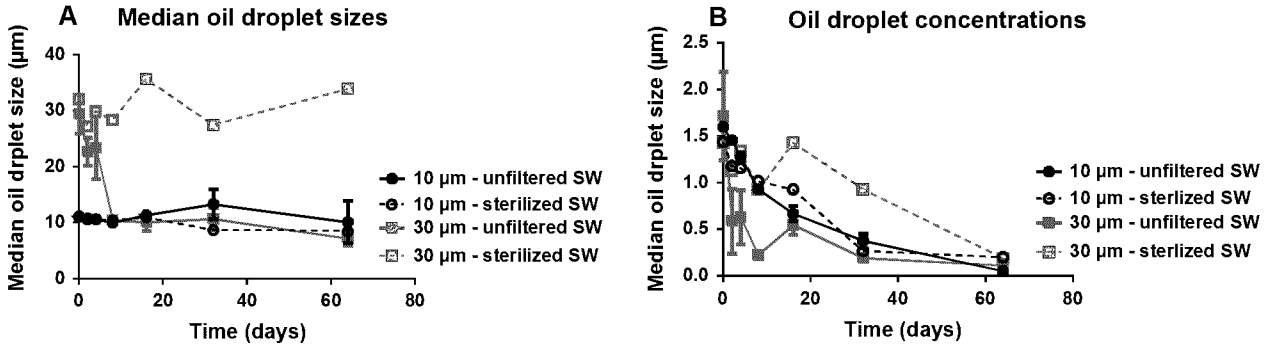


Fig. 2. Median oil droplet sizes (A) and concentrations (B) in oil dispersions generated during a biodegradation period of 64 days at 5 fC in natural unfiltered seawater (unfiltered SW), or in filtered (0.1 l m) and sterilized ($HgCl_2$) seawater (sterilized SW). The dispersions were generated at nominal particle sizes of 10 and 30 l m diameter. The dispersions in unfiltered seawater were analyzed in triplicate (error bars show standard deviation), while sterile samples were analyzed as single samples.

seawater experienced a rapid decline in droplet size between days 0 and 8, from 29.4 to 10.4 l m in average diameter (3 replicates), with a subsequent particle size between 10.2 and 13.4 l m median in the period from day 8 to 64. In contrast, the median oil droplet diameter was maintained in the sterile 30 l m dispersions, ranging from 27.2 to 34.9 l m during the experimental period (Fig. 2A). When oil droplet concentrations were determined by Coulter Counter analyses the concentrations declined more rapidly in natural unfiltered seawater than in the sterilized dispersions. In the 10 l m dispersions the concentrations were decreased from days 0 to 8 by 41.9% (from 1.60 to 0.93 mg/L average values) in natural unfiltered seawater and by 29.2% (from 1.44 to 1.02 mg/L) in the sterilized dispersions, while the reductions in the 30 l m dispersions were 86.9% (from 1.72 mg/L to 0.22 mg/L) and 35.0% (from 1.43 mg/L to 0.93 mg/L) in unfiltered and sterilized seawater, respectively (Fig. 2B). In the sterilized systems with 30 l m oil droplets it was evident that the larger droplets were removed faster than the smaller droplets (Supplementary Information, Fig. S4D). Reduced concentrations of droplets may therefore be caused by removal of the larger droplets with the fastest rising velocities or by droplet coalescence, generating droplets of sizes outside the measuring range of the Coulter Counter instrument (5.6–100 l m), as shown in oil droplet coalescence models (Sterling et al., 2004). The 10 l m dispersions also included oil droplets smaller than the lower instrumental measuring size of 5.6 l m (Supplementary Information, Figs. S4A and S4B). In addition, oil droplets could be removed from the system by attachment to the glass walls of the flasks, as measured by chemical analyses (see below). The higher reduction in oil droplet concentrations in unfiltered than sterilized dispersions may be caused by integration of droplets in "clusters" or "flocs" in natural seawater, which were visually observed in the experiment. These aggregates have been observed in several biodegradation studies of dispersed oil (e.g. Swannell et al., 1997; Harris et al., 2002; MacNaughton et al., 2003; Bælum et al., 2012).

### 3.2.2. Biodegradation of targeted oil compounds

Concentrations of 183 targeted semivolatile or volatile oil compound measured by GC–MS analyses showed that 81.4% of these were detected in the dispersions above the LOD (0.01 l g/L) at the start of the experiment. Compounds not detected above LOD included $C_0$–$C_4$ phenols and benzothiophenes (Supplementary Information, Fig. S5), while additional 13 compounds (7.1%) with concentrations close to LOD (60.1 l g/L) were excluded for biodegradation determination (Supplementary Information, Fig. S5).

Depletion of semivolatile $nC_{10}$–$nC_{36}$ alkanes and non-alkylated and alkyl-substituted decalines, naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, fluoranthenes and chrysenes were examined in the dispersions after normalization against the persistent biomarker 17a(H),21b(H)-Hopane (30ab Hopane), commonly used in biodegradation studies (Prince et al., 1994; Page et al., 1995; Wang et al., 1998). The depletions were determined as percentages of normalized data at the start of the experiment (day 0) for each target oil compound (Fig. 3). In average, the oil compound groups showed low to negligible depletion in sterilized dispersions during the first 32 days (average <1%), although decaline concentrations were reduced by more than 20%. After 64 days the oil compounds were further depleted in the sterilized dispersions (average reduction of 19%). However, compounds in natural unfiltered seawater were mostly reduced to near completion before they were depleted in the sterilized dispersions. The oil compound depletion in natural unfiltered seawater was therefore mainly the result of biotransformation.

Low-range ($nC_{10}$–$nC_{15}$) and medium-range ($nC_{16}$–$nC_{21}$) molecular weight (MW) n-alkanes were rapidly biotransformed after 4 days in the 10 l m dispersions (76.3 ± 2.7 and 74.5 ± 1.9% depletion, respectively), while biotransformation of these n-alkanes started later in the 30 l m dispersions and did not become evident until 8 days (84.2 ± 4.6 and 82.2 ± 3.4% degradation, respectively) in the 30 l m dispersions (Fig. 3A). Faster biotransformation of the low-range and medium-range MW n-alkanes was therefore measured in the 10 l m than the 30 l m dispersions. Also decaline biotransformation started faster in the smaller droplet dispersions, between days 8 and 16 in 10 l m dispersions (60.6 ± 3.6% degradation), and between days 16 and 32 (88.7 ± 9.5% degradation at 32 days) in the 30 l m dispersions (Fig. 3A). However, high-range MW n-alkanes ($nC_{22}$–$nC_{36}$) shower slower and more similar biotransformation in the two dispersions (73.0 ± 4.8 and 63.5 ± 0.5% degradation in the 10 l m and 30 l m dispersions after 16 days)(Fig. 3A).

Low-range and medium-range MW PAH-compounds (2- to 3-ring PAH) were biotransformed between day 8 and 16 in both dispersions, with 99.7 ± 0.2 and 88.9 ± 9.0% degradation after 16 days in the 10 and 30 l m dispersions, respectively (Fig. 3B). Also for these PAH compounds faster biodegradation in the 10 l m than the 30 l m oil droplet dispersions was indicated. However, larger PAH (4- to 5-ring) were only biotransformed between 32 and 64 days, with 95.7 ± 5.2 and 88.7 ± 2.1% decay in the 10 and 30 l m dispersions after 64 days.

VOC compounds determined by P&T GC–MS analyses could not be normalized against a biomarker, since analyses of these did not include any recalcitrant biomarker. Determination of % concentrations relative to 0-day concentrations for the alkane and aromatic VOC compound groups showed biotransformation mainly between 8 and 16 days, resulting in 99.6 ± 0.05 and 96.5 ± 5.0% depletion of

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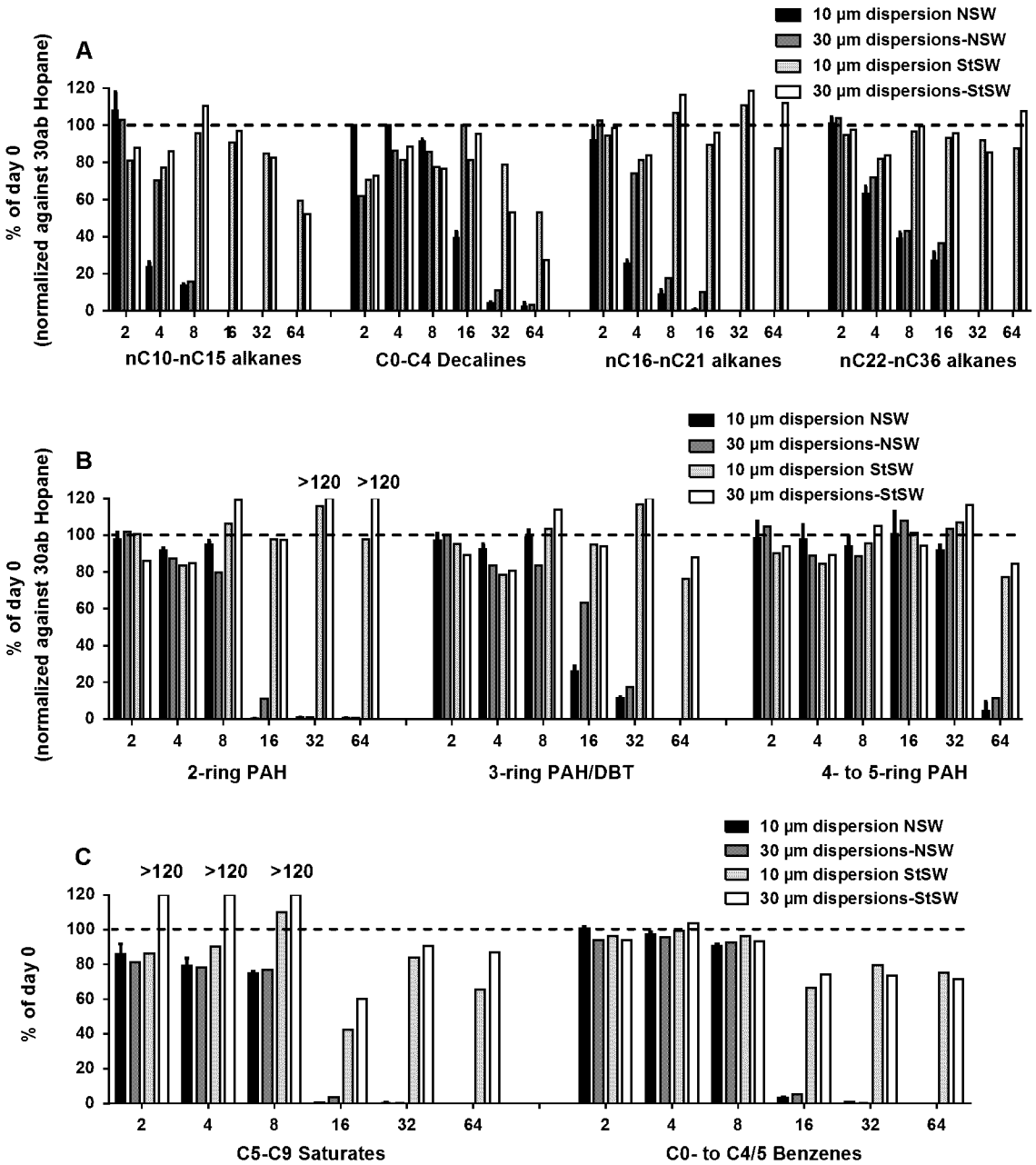


Fig. 3. Percentage concentrations compared to day 0 of semivolatile n-alkanes and $C_0$–$C_4$ alkylated decalines (A), semivolatile 2–5 ring PAH (B), and volatile alkanes and aromatic hydrocarbons (C) in 10 l m and 30 l m dispersions in natural seawater (NSW) and sterilized seawater (StSW) during an incubation period of 64 days, with samples collected after 2, 4, 8, 16, 32 and 64 days. The percentages of semivolatile compounds were determined from GC–MS analyses (triplicate) normalized against the biomarker 30ab Hopane with standard deviation error bars of 3 replicates. Volatile compounds were determined without normalization. The broken line shows the 0-day 100% for each target compound.

$C_5$–$C_9$ alkanes in 10 l m and 30 l m dispersions, respectively, while corresponding data for $C_0$- to $C_4$/$C_5$ benzenes were 96.8 ± 0.5 and 94.4 ± 2.3% depletion (Fig. 3C). Although sterilized dispersions also showed decreased concentrations of volatiles after 16 days (39.7–57.7% and 25.9–33.5% depletion of saturates and benzenes, respectively) most of the depletion in natural unfiltered seawater may therefore be accounted for by biodegradation.

Non-linear regression analyses of single oil compounds (normalized against 30ab Hopane) were performed by 1st order rate kinetics not including the determined lag-phases, and rate coefficients and half-lives for targeted oil compounds were determined in the dispersions. Low oil concentrations with no significant increase in microbial concentrations (epifluorescence microscopy) during the biodegradation period (average cell numbers differed with a factor of 1.02 between days 0 and 64) argued for 1st order kinetics to determine biotransformation coefficients and half-lives (Battersby, 1990). Non-responsive periods (lag-phases) were observed for most of the targeted compounds (Fig. 3). During the DWH spill it was suggested that deepwater with bacteria re-entered the spill site and caused accelerated hydrocarbon biodegradation (Valentine et al., 2012), resulting in a situation in which hydrocarbon-stimulated bacterial populations eventually could degrade oil compounds without a preceding lag-phase.

First-order rate calculations of targeted semivolatile n-alkanes and 2- to 4-ring PAH normalized against 30ab Hopane were performed (Fig. 4, Table S2). Half-lives calculated from the rate

coefficients varied from 0.6–5.6 days (median 1.1 days) and 1.1–11.1 days (median 2.5 days) for $nC_{10}$–$nC_{30}$ alkanes in 10 lm and 30 lm dispersions, respectively, while corresponding data for 2- to 4-ring PAH were 0.9–31.9 (median 5.3 days) and 0.9–54.9 days (median 10.2 days). The half-lives for most of the targeted compounds (44 of 48 compounds) were lower in the 10 lm than the 30 lm dispersions, and the differences between the dispersions were significant ($P < 0.05$; Wilcoxon non-parametric t-test). The n-alkane half-lives were increased with longer carbon-chains in both dispersions, primarily in the high-boiling-point range (P $nC_{21}$). PAH half-lives increased in both dispersions with increasing numbers of aromatic rings and with degree of alkyl-substitution, except for the chrysenes (Fig. 4). Only small differences in half-lives were determined for chrysenes, which appeared in low concentrations in the dispersions (sum of $C_0$–$C_4$ chrysenes of 0.59 and 0.79 lg/L in 10 lm and 30 lm dispersions, respectively; supplementary information Fig. S5). Small oil droplets therefore had a positive impact on biotransformation of both n-alkanes and PAH. In a recent study of Macondo oil biodegradation under a near-surface temperature relevant for the GoM, comparing physically and chemically dispersed oil, we observed higher biodegradation differences related to droplet size for n-alkanes ($nC_{10}$–$nC_{30}$) than 2- to 4-ring PAH (Brakstad et al., 2014). However, in the near-surface oil biodegradation study both temperature (30–32 fC), experimental system and oil droplet size distributions differed from the current experiment. The different temperatures will also stimulate different taxa of oil-degrading bacteria, as shown from field analyses of the DWH incident, in which none of the predominant bacteria in the deepwater plume (Oceanospirillales, Colwellia and Cycloclasticus) were abundant in surface slicks (Redmond and Valentine, 2012). Detailed results from characterization of cell counts and bacterial communities from the current study will be presented in a separate manuscript (Brakstad et al., in preparation). And importantly, the oil characteristics will be different at the two temperatures. For instance some of the larger n-alkanes may generate wax crystals at low temperature, thereby becoming less susceptible to biodegradation.

First-order rates are often calculated without accounting for the lag-phases. In these studies the lag-periods become a part of the half-live determination. In Table S2 (Supplementary Information) the half-lives are also determined as the sum of the lag-periods and the half-lives determined from the rate coefficients. By these calculations the n-alkane half-lives varied from 2–17.6 days in the 10 lm dispersions and 3.1–20.8 days in the 30 lm dispersions. PAH half-lives varied correspondently from 8.8–49.9 and 8.7–79.9 days in the two dispersions. The same trends for n-alkanes and PAH were observed with these half-life calculations as described above, with generally shorter half-lives of the same compounds in the 10 lm than in the 30 lm dispersions. The sums of half-lives and lag-phases also differed significantly between the 10 lm and the 30 lm dispersions ($P < 0.05$; Wilcoxon non-parametric t-test).

Our n-alkane and PAH biodegradation data, using coastal Norwegian seawater from 80 m depth, mainly coincided with results from studies with chemically dispersed oils incubated at low temperature (L 1 to +8 fC), in which n-alkane depletion corresponded to half-lives of 2 to approximately 10 days, while 2- to 4-ring half-lives ranged between 2 and 37 days (Siron et al., 1995; Venosa and Holder, 2007; Prince et al., 2013; McFarlin et al., 2014). Also results from the DWH deepwater plume samples and laboratory studies with microbial consortia or seawater from GoM indicated average n-alkane ($nC_{13}$-$nC_{26}$) half-lives of 1.2–6.1 days (Hazen et al., 2010), showing good agreement with our results. In a recent study with small droplet (10–30 lm) dispersions of Macondo oil in GoM deepwater, biotransformation of 2–3 ring PAH appeared mainly between 9 and 39 days of incubation, while 4–6 ring PAH

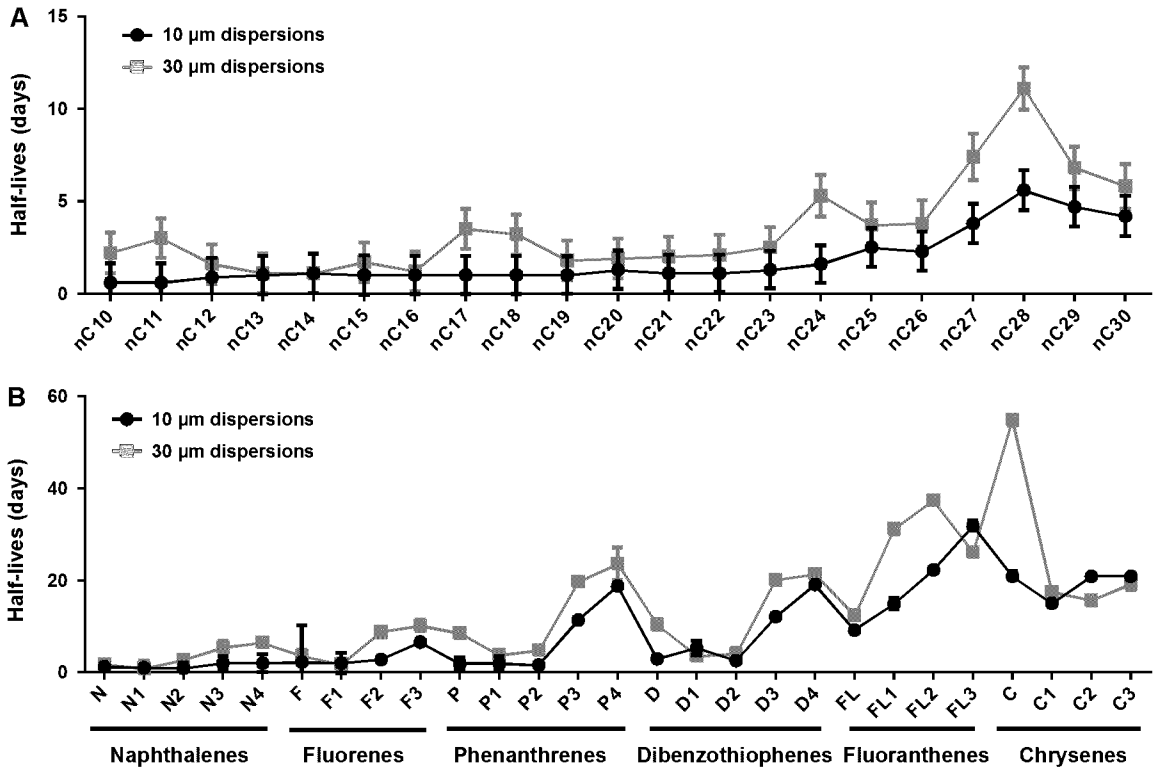


Fig. 4. Half-lives of $nC_{10}$–$nC_{30}$ alkanes (A) and naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, fluoranthenes and chrysenes (B) in 10 lm and 30 lm dispersions with standard deviation errors bars of 3 replicates. Half-lives were determined from rate coefficients without lag-periods included. The numbering of the aromatic groups describes the degree of alkyl-substitution.

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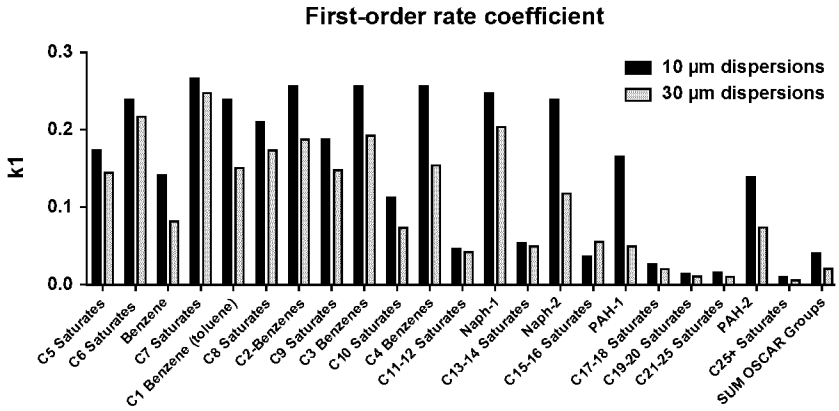


Fig. 5. First-order rate coefficients for oil compound groups of the Macondo oil in 10 and 30 l m dispersions.

transformation had started after 39 days of incubation (Wang et al., 2014), consistent with PAH results from our study.

Oil compound glass wall attachment is well known, and comparison of oil concentrations (TEOC analyses) in water and on glass walls rinsed with solvent (days 0, 8 and 32) showed a gradual increase of wall-attached material, from <3% of total TEOC (day 0), to up to 45% (30 l m dispersions at day 32). Targeted analyses of compounds normalized against 30ab Hopane showed relative preference of 2-ring and non-alkylated 3-ring PAH for the water-phase, while larger alkylated 3-ring and 4- to 5-ring PAH, decalines and n-alkenes gradually distributed between the water- and glass-phase (results not shown). These data emphasize that degradation of dispersed oil in laboratory systems is a result of processes in both water and glass wall surfaces.

### 3.2.3. Biodegradation of oil compound groups

The well-known targeted compounds described above only cover a fraction of the oil. Comparison of TEOC concentrations (GC-FID analyses) with the targeted SVOC and VOC saturate and aromatic oil compound (GC–MS analyses) showed that the sum of the targeted compounds (n-alkenes, 2–5 ring PAH, volatile $C_5$–$C_9$ saturates and $C_0$–$C_5$ benzenes) constituted 33.5% and 40.4% of the sum of TEOC and VOC concentration at the start of the experiment in the 10 l m and 30 l m dispersions, respectively (Supplementary Information, Fig. S6). The TEOC concentrations determined by GC-FID analyses represented 72% and 81% of the oil droplet concentrations measured by the Coulter Counter analyses for the two dispersions, and these results corresponded well with the assumption from true boiling point curves, assuming that $C_5$–$C_{36}$ saturates (boiling points of 27 to approximately 500 fC) represent 70–80% of typical crude oil (Pasquini and Bueno, 2007).

Biotransformation rate coefficients and half-lives of 22 volatile and semivolatile oil compound groups, representing the boiling point range described above (Table S1) were calculated, including $C_5$–$C_{36}$ saturates and 1- to 5-ring aromatic compounds (Reed et al., 2000). The results of Fig. 5 and Table S3 showed rate coefficients of 0.0096–0.2665 (median 0.1692) in the 10 l m dispersions and 0.0054–0.2475 (median 0.0995) in the 30 l m dispersions. These rates resulted in half-lives of 2.8 to 72.2 days (median 4.1 days) and 2.8 to 128.3 days (median 7.2 days) in the 10 and

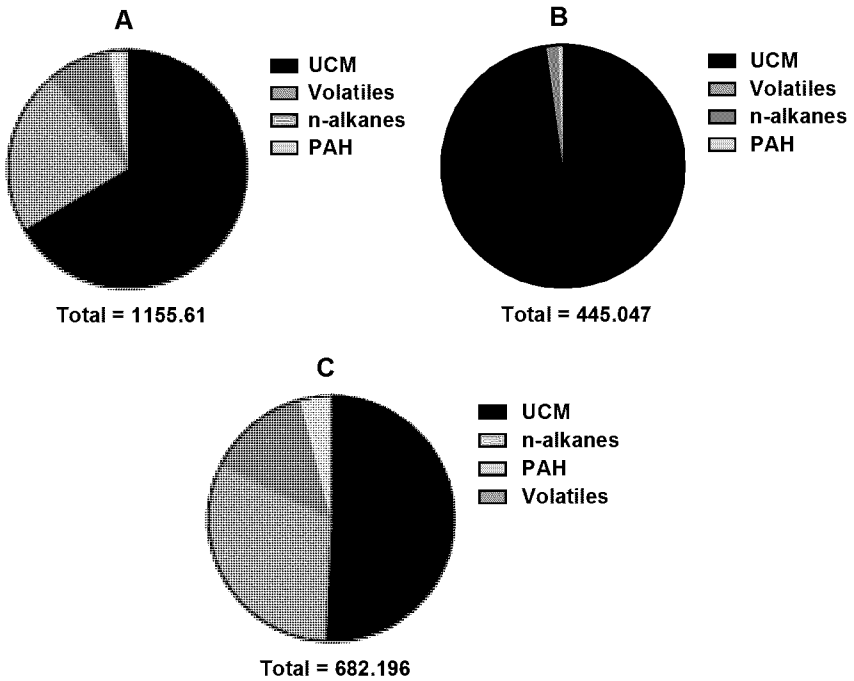


Fig. 6. Distributions of targeted oil compounds and UCM at the start of the biodegradation (A) and after 32 days of incubation in unfiltered (B) and sterilized (C) dispersions. The total concentrations of TEOC (l g/L) are shown below each pie chart.

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30 l m dispersions, respectively. The rate coefficients were higher in the 10 l m than the 30 l m dispersions for all oil compounds, except for $C_{15}$–$C_{16}$ saturates. Comparison of the rate coefficients in the two dispersions showed significant differences ($P < 0.05$; Wilcoxon non-parametric t-test). The rate coefficients were higher in favor of the 10 l m dispersions by factors of 1.21 and 1.67 (median values) for the saturate and aromatic compound groups, respectively. The rate coefficients were generally higher for the aromatic (average of 0.175039) than the saturate (0.099304) oil compound groups when data from both dispersions were compiled. This is probably associated with the water-solubility of the aromatic hydrocarbons, as well as the presence of poorly biodegradable branched and cyclic alkanes in the semivolatile saturate groups.

In previous studies we have compared dissolution and biodegradation of oil compounds from thin oil films (10–20 l m thickness) immobilized on hydrophobic adsorbents, showing that fast dissolution of naphthalenes and non-alkylated 3-ring PAH resulted in biodegradation mainly of dissolved compounds, while negligible dissolution of n-alkanes ($nC_{12}$–$nC_{36}$) resulted in biodegradation of these compounds exclusively on the oil–water interphases. For the larger PAH-compounds dissolution decreased with increasing numbers of aromatic rings and alkyl substitution, with biodegradation of these both as dissolved and as oil-associated compounds (Brakstad et al., 2004; Brakstad and Bonaunet, 2006). Oil compound biodegradation is therefore a complex process, involving bacterial communities in the water-phases as well as bacteria attaching the oil surfaces.

The rate for the sum of the 22 oil compound groups in this study was also faster in the 10 l m ($k1 = 0.03984$) than the 30 l m ($k1 = 0.02004$) dispersions, resulting in half-lives of 17.4 and 34.6 days in the two dispersions (Fig. 5; Table S3). Since the sum of these groups may represent most of the oil, these numbers may be used as biotransformation rates for the oil. The oil droplet size was therefore important both for the biotransformation rates of the oil compound groups and the sum of these groups used in this study and presenting a boiling point range of 27–>500 fC.

The saturates representing the $C_{10}$ to $C_{25+}$ oil compound groups are mostly unidentifiable oil compounds, often termed as the unresolved complex mixture (UCM) (Gough and Rowland, 1990; Killops and Al-Juboori, 1990), and accounts for 60–70% of the groups. Comparison of the sum of TEOC and VOC concentrations with targeted compound groups of n-alkanes, PAH and volatile hydrocarbons showed that the UCM became the predominant oil fraction during the biodegradation period (Fig. 6; Fig. S6, Supplementary Information). Several studies have shown that the UCM fraction includes compounds that are not readily susceptible to biodegradation (Reddy et al., 2002; Booth et al., 2007). The UCM was predominant in each of the saturate groups from $C_{11}$–$C_{12}$ to $C_{25+}$ (Table S1). The degradation of these compounds decreased by increasing boiling point ranges in both 10 l m and 30 l m dispersions (Table S3), and the rate calculations showed that their degradation was mainly faster in the 10 l m than the 30 l m dispersions (Fig. 5; Table S3).

The result from the current study show that reduced oil droplet sizes resulted in increased biodegradation rates. The use of chemical dispersants will generate small droplet oil dispersions, and the result from this and other studies (e.g. Siron et al., 1995; Venosa and Holder, 2007.; Prince et al., 2013; McFarlin et al., 2014; Brakstad et al., 2014) demonstrate that the use of dispersants to generate small droplets will promote biodegradation in seawater at different environmental conditions. Dispersants like Corexit 9500 are considered to have moderate to low acute toxicity (e.g. Mitchell and Holdway, 2000; Judson et al., 2010), and surfactants like alkyl sulfosuccinates may be biodegradable (Garcia et al., 2009; Bælum et al., 2012). The positive influence of chemical dispersants on the biodegradation of potentially toxic oil compounds may therefore compensate for possible negative effects of dispersant components in the marine environment.

Operationally, dispersants have mainly been used for surface oil spills to remove the slick from the seawater surface by generation of small droplet dispersions in the water column. We have previously shown that oil compounds in surface oil emulsions are poorly biodegradable compared to chemically dispersed oil (Brakstad et al., 2014). The dispersant application during the DWH incident aimed at reducing surface slick generation and may also have contributed to the generation of the small oil droplets in the Macondo deepwater plume. If deepwater injection of dispersant during an oil spill is able to reduce oil droplet size and avoid oil surfacing, this may enhance oil compound biodegradation and thereby additionally reduce the impacts of the spill. However, it is important to emphasize the lack of knowledge related to the many unidentifiable oil compounds, both with respect to biodegradability and toxic effects.

Although the water used in the current study was Norwegian coastal seawater, the results may be related to the Macondo deepwater plume. Both oil, oil droplet size distribution (North et al., 2011) and seawater temperature was similar in the current experiment and the DWH deepwater plume. Our experiments were performed at atmospheric pressure, but laboratory experimental studies have shown that bacteria associated with deepwater plume biodegradation of the Macondo oil also biodegraded the oil at atmospheric pressure (Hazen et al., 2010; Bælum et al., 2012).

## 4. Conclusions

The study presented here compares, for the first time to our knowledge, biodegradation rates in oil dispersions with pre-defined droplet sizes, and under temperatures relevant for a deepwater discharge. The results of this study showed that biodegradation of alkane and aromatic hydrocarbons in a dispersible oil (Macondo) was faster in 10 l m than 30 l m dispersions for targeted oil compounds and oil compound groups, as well as the sum of the groups representing most of the oil. These data indicate that dispersant treatment of deepwater oil spills will be beneficial for the oil compound biodegradation, if oil droplet sizes are reduced. Our data showed good agreement with results from other biodegradation studies performed with chemically dispersed oil at low seawater temperatures. Although the current study was performed in seawater from a Norwegian fjord and under atmospheric pressure, these data may also have relevance for the DWH deepwater oil plume. We used the same oil, similar temperatures (4–5 fC), and oil droplet size distributions were comparable to the DWH deepwater plume. Published oil compound degradation data with GoM seawater or enrichment cultures also showed agreement with our results. Comparison of fate model predictions, laboratory results and field data may further substantiate the fate of oil dispersions in deepwater spills and improve the information concerning the impacted deepwater area of a spill. This information is important to include in risk assessment analyses.

## Acknowledgments

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.marpolbul.2015.02.006.

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RESEARCH TRANSPARENCY

# Why null results rarely see the light of day

## "File drawer" study proposes registry for unpublished social science data

By Jeffrey Mervis

Researchers have put numbers on the "file drawer" phenomenon, in which scientists abandon results that they believe journals are unlikely to publish.

In a study published online this week in *Science* (http://scim.ag/AFranco), a team at Stanford University in Palo Alto, California, traced the publication outcomes of 221 survey-based experiments funded by the National Science Foundation. Nearly two-thirds of the social science experiments that produced null results, those that did not support a hypothesis, were simply filed away. In contrast, researchers wrote up 96% of the studies with statistically strong results (see graph).

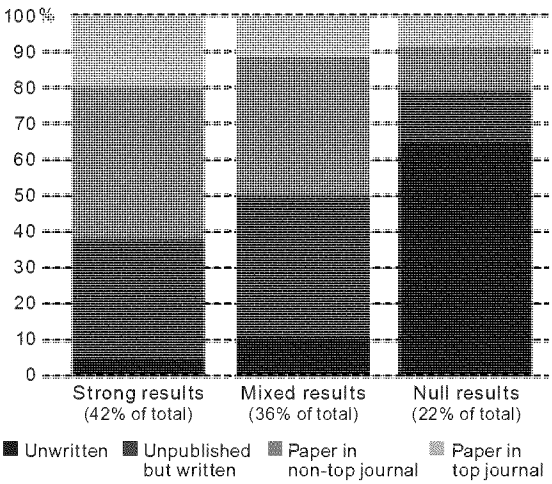
Such practices can skew the literature and lead to wasteful duplication, the authors argue. Their remedy: Deposit all data and study designs into public registries. But while most scientists agree that a registry would be valuable, some worry that it would become burdensome and could even introduce new biases. "I wouldn't want to take all the unpublished findings and give them the same prominence as those containing strong results," says political scientist Gary King of Harvard University.

The question of what to do with null results—when researchers fail to see an effect that should be detectable—has long been hotly debated among those conducting medical trials, where the results can have a big impact on lives and corporate bottom lines. More recently, the debate has spread to the social and behavioral sciences, which also have the potential to sway public and social policy. There were little hard data, however, on how often or why null results were squelched. "Yes, it's true that null results are not as exciting," King says. "But I suspect another reason they are rarely published is that there are many, many ways to produce null results by messing up. So they are much harder to interpret."

In the new study, Stanford political economist Neil Malhotra and two of his graduate students examined every study since 2002 that was funded by a competitive grants program called TESS (Time-sharing Experiments for the Social Sciences). TESS allows scientists to order up Internet-based surveys of a representative sample of U.S. adults to test a particular hypothesis (for example, whether voters tend to favor legislators who boast of bringing federal dollars to their districts over those who tout a focus on policy matters).

**Most null results are never written up**

The fate of 221 social science experiments




Source: A. Franco *et al.*, *Science* (28 August)

Malhotra's team tracked down working papers from most of the experiments that weren't published, and for the rest asked grantees what had happened to their results. In their e-mailed responses, some scientists cited deeper problems with a study or more pressing matters—but many also believed that journals just wouldn't be interested. "The unfortunate reality of the publishing world are that null effects do not tell a clear story," said one scientist. Said another, "Never published, definitely disappointed to not see any major effects."

Their answers suggest to Malhotra that rescuing findings from the file drawer will require a shift in expectations. "What needs to change is the culture—the author's belief about what will happen if the research is written up," he says.

Not unexpectedly, the statistical strength of the findings made a huge difference in whether they were ever published. Overall, 42% of the experiments produced statistically significant results. Of those, 62% were ultimately published, compared with 21% of the null results. However, the Stanford team was surprised that researchers didn't even write up 65% of the experiments that yielded a null finding.

Scientists not involved in the study praise its "clever" design. "It's a very important paper" that "starts to put numbers on things we want to understand," says economist Edward Miguel of the University of California, Berkeley.

He and others note that the bias against null studies can waste time and money when researchers devise new studies replicating strategies already found to be ineffective. Worse, if researchers publish significant results from similar experiments in the future, they could look stronger than they should because the earlier null studies are ignored. Even more troubling to Malhotra was the fact that two scientists whose initial studies "didn't work out" went on to publish results based on a smaller sample. "The non-TESS version of the same study, in which we used a student sample, did yield fruit," noted one investigator.

A registry for data generated by all experiments would address these problems, the authors argue. They say it should also include a "preanalysis" plan, that is, a detailed description of what the scientist hopes to achieve and how the data will be analyzed. Such plans would help deter researchers from tweaking their analyses after the data are collected in search of more publishable results.

Some researchers are wary. Requiring a preanalysis plan, for instance, could breed resentment, says James Coan, a social psychologist at the University of Virginia in Charlottesville. "It's part of a scientist's job to be canny enough" to do the most appropriate statistical analyses, he says. "The implicit message is that scientists are not to be trusted with those decisions."

Miguel, a member of the recently formed Berkeley Initiative for Transparency in the Social Sciences, is one of many who say a registry should be encouraged, but not imposed. "We want the community to adopt good norms, and then promote them," he says. "That's certainly the most attractive outcome." ■

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V and G,

Pursuant to our discussion on the phone last week, have you ever read my article in ES&T about the biodegradation of SLC with and without C9500 in our lab microcosms (attached)? If not, or even if you have but forgot the Discussion, open the article and read lines 327 to 483, especially lines 397 to 429. Even though Pablo was lead author, I was the one who contributed the interpretation of much of our results, and I don't know if anyone has ever referred to it in post-publication articles as I've been away too long. Greg, since you are a gearhead, I'm sure you know all about Fick's Law of Diffusion. Check it out and lemme know your thoughts. I will be paraphrasing this text in the Royal Society of Canada (RSC, similar to our own NAS) panel that is writing a book on the effects of oil spills in different environments.

AV

**To:** kathy.mandsager@unh.edu[kathy.mandsager@unh.edu]; conmy.robyn@gmail.com[conmy.robyn@gmail.com]; fingasmerv@shaw.ca[fingasmerv@shaw.ca]; tchazen@utk.edu[tchazen@utk.edu]; robert.jones@noaa.gov[robert.jones@noaa.gov]; mandyjoye@gmail.com[mandyjoye@gmail.com]; ken.lee@csiro.au[ken.lee@csiro.au]; mbleigh@alaska.edu[mbleigh@alaska.edu]; karl.linden@colorado.edu[karl.linden@colorado.edu]; kmmcfarlin@alaska.edu[kmmcfarlin@alaska.edu]; msmiles@lsu.edu[msmiles@lsu.edu]; thomas.s.coolbaugh@exxonmobil.com[thomas.s.coolbaugh@exxonmobil.com]; Sprenger, Mark[Sprenger.Mark@epa.gov]
**Cc:** Wilson, Gregory[Wilson.Gregory@epa.gov]; Principe, Vanessa[Principe.Vanessa@epa.gov]; Peter.Kinner@unh.edu[Peter.Kinner@unh.edu]; nancy.kinner@unh.edu[nancy.kinner@unh.edu]; tracee.nguyen@csiro.au[tracee.nguyen@csiro.au]
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Dear group members,

Find attached a new paper (in press) from SINTEF that shows that reduced oil droplet size gives increased biodegradation of oil.

This work was mentioned during our sessions but is now also published.

Regards,

Mathijs

Mathijs G.D. Smit - PhD
Environmental Scientist
Shell Global Solutions International BV

**Tel:** +31-70-447-5234
**Mob:** +31-6-4681 9522
**Fax:** +31-70-447-8059
**Email:** mathijs.smit@shell.com

**Visitor address:** Lange Kleiweg 40, 2288 GK, Rijswijk , The Netherlands
**Postal address:** PO Box 60, 2280 AB Rijswijk, The Netherlands
**Internet:** www.shell.com/globalsolutions

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**Sent:** 23 February 2015 21:05
**To:** 'Robyn Conmy <conmy.robyn@gmail.com> (conmy.robyn@gmail.com)'; 'fingasmerv@shaw.ca'; 'tchazen@utk.edu'; 'Robert Jones - NOAA Federal'; 'Samantha Joye'; 'ken.lee@csiro.au'; 'mbleigh@alaska.edu'; 'karl.linden@colorado.edu'; 'kmmcfarlin@alaska.edu'; 'msmiles@lsu.edu'; 'thomas.s.coolbaugh@exxonmobil.com'; Smit, Mathijs GD GSNL-PTS/TESC; 'Sprenger, Mark <Sprenger.Mark@epa.gov> (Sprenger.Mark@epa.gov)'
**Cc:** 'Wilson, Gregory'; 'Principe, Vanessa'; Kinner, Peter; Kinner, Nancy; 'tracee.nguyen@csiro.au'
**Subject:** Grp 3: degradation & fate state of science follow-up meeting

As Ian & Lindsey of CRRC complete their task of creating a new spreadsheet with information from the older published papers (LUMCON) that address biodegradation, I'd like to schedule another Group 3 meeting to discuss and finalize these potential findings.

Please let me know if you can possibly be available for a 2-hour meeting via WebEx on:

Wednesday 3/11 at 1:30 EST

Thursday 3/12 at 1:00 EST

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Kathy Mandsager

Program Coordinator

Coastal Response Research Center

Center for Spills in the Environment

234 Gregg Hall, Colovos Rd

University of New Hampshire

Durham, NH 03824

603.862.1545

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# Biodegradation of dispersed Macondo oil in seawater at low temperature and different oil droplet sizes

Odd G. Brakstad ⇑, Trond Nordtug, Mimmi Throne-Holst

SINTEF Materials and Chemistry, Environmental Technology, Dept. Applied Environmental Biology and Chemistry, N-7465 Trondheim, Norway

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During the Deepwater Horizon (DWH) accident in 2010 a dispersant (Corexit 9500) was applied at the wellhead to disperse the Macondo oil and reduce the formation of surface slicks. A subsurface plume of small oil droplets was generated near the leaking well at 900–1300 m depth. A novel laboratory system was established to investigate biodegradation of small droplet oil dispersions (10 lm or 30 lm droplet sizes) of the Macondo oil premixed with Corexit 9500, using coastal Norwegian seawater at a temperature similar to the DWH plume (4–5 ffC). Biotransformation of volatile and semivolatile hydrocarbons and oil compound groups was generally faster in the 10 lm than in the 30 lm dispersions, showing the importance of oil droplet size for biodegradation. These data therefore indicated that dispersant treatment to reduce the oil droplet size may increase the biodegradation rates of oil compounds in the deepwater oil droplets.

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## 1. Introduction

During the Deepwater Horizon (DWH) incident some of the oil was dispersed as small droplets in the deep ocean at depths of 900–1300 m near the leaking well, and at water temperatures of 4–6 ffC (Camilli et al., 2010; Reddy et al., 2012). Simulations of the plume trajectories predicted that oil droplets with diameters between 10 and 50 lm would form in a distinct subsurface layer and be transported horizontally, while droplets larger than 90 lm rapidly rose to the surface (North et al., 2011). Samples from the deepwater plume showed enrichment of water-soluble components (Camilli et al., 2010). Measurements of PAH in water samples during the release showed rapid decrease with distance from the release point. The responders began injecting the chemical dispersant Corexit 9500A at the wellhead in early May 2010 to reduce the amount of oil that formed surface slicks and reached the Gulf of Mexico (GoM) coastlines (Atlas and Hazen, 2011; Kujawinski et al., 2011). In addition, surface operations included mechanical recovery techniques and application of the chemical dispersants Corexit 9527 and 9500A (Coastal Response Research Center, 2010).

It was early observed that the deepwater plume stimulated bacteria associated with hydrocarbon biodegradation in cold seawater (Oceanospirillaceae, Pseudomonas, Cycloclasticus, Colwellia, Pseudoalteromonas, Methylophaga) (Valentine et al., 2010; Hazen et al., 2010; Redmond and Valentine, 2012; Dubinsky et al., 2013), and data from the field and from laboratory experiments indicated short biodegradation half-lives for $nC_{13}$–$nC_{26}$ alkanes, ranging from 1 to 8 days (Hazen et al., 2010). A sequential and pulsed propagation of bacteria degrading specific hydrocarbons was suggested, including n-alkanes, aromatics and $C_1$–$C_3$ gas components (Valentine et al., 2012; Dubinsky et al., 2013). Results from stable isotope analyses reported that close to 70% of the oxygen consumption in the deepwater plume was related to bacterial respiration of propane and ethane (Valentine et al., 2010), while methane oxidation was delayed (Valentine et al., 2010; Kessler et al., 2011).

Biodegradation rates of components in dispersed oil are normally expected to increase when oil droplet size is reduced, for instance by treatment of the oil with chemical dispersants. Smaller droplets will generate larger oil–water interphase areas for the oil-degrading bacteria to attach to, and dissolution of water-soluble compounds will increase. Volatile oil compounds will rapidly dissolve during subsurface spills and thereby become subject to biodegradation. In contrast volatiles will largely evaporate after surface spills. Several laboratory studies have shown that dispersant treatment of dispersible oils increase oil compound biodegradation (Siron et al., 1995; Venosa and Holder, 2007; Prince et al., 2013; McFarlin et al., 2014; Brakstad et al., 2014).

To our knowledge, no laboratory studies have attempted to relate the biodegradation of oil compounds to measured droplet sizes in the dispersions. We therefore established a novel

⇑ Corresponding author. Tel.: +47 98243447; fax: +47 73597043.
E-mail address: odd.brakstad@sintef.no (O.G. Brakstad).

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experimental system for comparing oil dispersions of different small droplet sizes in natural seawater. This system was based on combining an oil dispersion generator (Nordtug et al., 2011) and a slowly rotating carousel system to generate small droplet dispersions and avoid droplets rising to the surface. The primary aim of our study was therefore to quantify biodegradation of hydrocarbons in dispersions with defined oil droplet sizes relevant for chemically dispersed oil, and at low seawater temperatures, corresponding to deepwater discharges. Biodegradation of chemically dispersed Macondo oil at two median oil droplet sizes (10 and 30 lm) in natural seawater at 4–5 ffC was investigated with this system. Norwegian coastal seawater was used in the study, but experimental conditions (oil, oil droplet size distributions and seawater temperature) were relevant to the DWH deepwater plume.

## 2. Materials and methods

### 2.1. Oil, dispersant and seawater used in experiments

Unweathered Macondo (MASS) oil was collected from a riser pipe connected to the well on 22 May 2010. COREXIT 9500A (Nalco, Sugar Land, TX) dispersant was used at a dispersant-to-oil ratio (DOR) of 1:100. Seawater was collected from a depth of 80 m (below thermocline) in a Norwegian fjord (Trondheimsfjord; 63ff26°N, 10ff23°E), outside the harbor area of Trondheim, the water is supplied via a pipeline system to our laboratories. The water source is considered to be non-polluted and not influenced by seasonal variations. The salinity of the seawater was 34‰, with a water temperature of 6–8 ffC and dissolved oxygen (DO) of approximately 8 mg/L when reaching our laboratory (Brakstad et al., 2004).

### 2.2. Oil dispersion generator and carousel system

An oil droplet generator was used for preparing oil dispersions with defined droplet size distributions, as previously described (Nordtug et al., 2011). The system consists of 3 chambers with an inner diameter of 8 mm connected by nozzles with a diameter of 0.5 mm. Oil dispersions with defined oil droplet size distributions and concentrations are generated by injecting oil via a capillary into a flow of seawater which moves through the chambers (Nordtug et al., 2011). Oil droplet concentrations and size distribution were determined by Coulter Counter analyses (see below). Flasks (2 L; Schott) were baked (450 ffC; 3 h) and soaked overnight (4% Deconex 11 Universal, Borer, Switzerland), washed with detergent (Neodisher N, Dr. Weigert, Germany), and thoroughly rinsed and autoclaved (121 ffC, 20 min) before use.

The flasks were completely filled with oil dispersions (no headspace or air bubbles) and mounted on a carousel system. During mounting of flasks and biodegradation experiments the wheels were slowly rotated around the carousel axis (0.75 r.p.m.) by a gear motor (SEW Eurodrive, Moss, Norway). In the main biodegradation experiment described here, four carousels with double sets of wheels, holding up to 16 flasks each, were used.

### 2.3. Biodegradation experiment

The MASS oil was heated at 50 ffC for 30 min, mixed by shaking for 3 min, and cooled to room temperature, after which it was mixed with the dispersant Corexit 9500A (DOR 1:100) at room temperature. This dispersant was shown to effectively disperse the Macondo oil (Daling et al., 2014). Pre-adaption of the seawater prior to the biodegradation experiments was conducted by diluting a stock dispersion (200 mg/L oil; oil droplet size 10 lm) to 0.2 mg/L Macondo oil (measured by Coulter Counter) in natural unfiltered seawater (pre-incubated over night at 5 ffC) in 2-L flasks completely filled (no air bubbles) with the dispersions, with incubation in the carousel system at 5 ffC for 5 days (rotation 0.75 r.p.m.). The experiment was then started by generating dispersions in the pre-adapted seawater with median oil droplet sizes of 10 lm or 30 lm and nominal oil concentration of 2 mg/L from a stock oil dispersion (200 mg/L oil) in natural unfiltered seawater. Dispersions of 10 lm or 30 lm median oil droplet sizes and 2 mg/L nominal concentrations were also prepared in sterile-filtered (0.2 lm) seawater (incubated at 4–5 ffC overnight before use) supplemented with $HgCl_2$ (100 mg/L), to minimize bacterial growth. Immediately after generation of dispersions flask were mounted on the carousel at slow rotation (0.75 r.p.m.). Flasks with experimental blank samples (unfiltered seawater without oil) were also included in the experiment for background analyses. Experiments were conducted at 5 ffC for up to 64 days. Flasks (triplicate samples; 2.3 L sample) of dispersions in natural seawater were sacrificed for analyses after 15 min on the carousel (0-day samples) and after 2, 4, 8, 16, 32, or 64 days of incubation on the carousels. One sterilized control flask and one experimental blank flask were also sacrificed for analyses at the each sampling point.

### 2.4. Analyses

#### 2.4.1. Oil droplet analyses

Oil droplet concentrations and size distributions were determined by Coulter Counter measure (Beckman Multisizer 4; Beckman Coulter Inc., Brea, CA, USA) fitted with either 100 lm or 280 lm apertures, for measurement of droplets within a diameter range of 2–60 lm or 5.6–100 lm, respectively. Filtered (0.22 lm) seawater was used as electrolyte. All median droplet sizes reported here are expressed as median droplets diameter on droplet volume if not otherwise mentioned.

#### 2.4.2. Chemical analyses

Samples of dispersions and seawater were solvent–solvent extracted with dichloromethane (DCM) for measurements of semivolatile organic compounds (SVOC) by gas chromatographic methods. The flask glass walls were also rinsed with DCM after removal of dispersions to extract material attached to the glass walls. All extracts were pooled before analyses. A gas chromatograph coupled to a flame ionization detector (GC-FID; Agilent 6890 N with 30 mDB1 column; Agilent Technologies) was used for quantification of extracted $C_{10}$–$C_{36}$ saturates separated according to boiling points, termed as total petroleum hydrocarbons extractable organic carbon (TEOC), while 96 individual targeted compounds ($C_{10}$–$C_{36}$ n-alkanes, decalines, phenols, 2- to 5-ring polyaromatic hydrocarbons (PAH) and 17a(H),21b(H)-Hopane (30ab Hopane) were analyzed in a gas chromatograph coupled to a mass spectrometer (GC–MS; Agilent 6890 plus GC coupled with an Agilent 5973 MSD detector, operated in Selected Ion Monitoring [SIM] modus; Agilent Technologies), as recently described (Brakstad et al., 2014). Dispersions were acidified (pH < 2) for analyses of 87 targeted volatile organic carbon (VOC) compounds in a Purge & Trap unit (Teledyne Tekmar Atomx; Mason OH, USA.) coupled to a GC–MS (Agilent 6890 N GC and an Agilent 5975B MSD detector; Agilent Technologies)(P&T GC–MS). The VOC and SVOC target compounds included in GC–MS analyses are shown in Table S1. The response values for individual target analytes were determined, with a signal-to-noise ratio of 10 as the lower detection limit, and a lower limit of detection (LOD) of 0.01 lg/L was defined for individual oil compounds.

#### 2.4.3. Temperature, dissolved oxygen, nutrients, and biomass

Air and seawater temperatures were logged through the experimental period. Dissolved oxygen was measured by a

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dissolved oxygen meter (YSI, Inc., Yellow Springs, OH). Nutrient analyses included $NO_3$–N + $NO_2$–N (ISO 13395), $NH_4$–N (ISO 11732), o-$PO_4$–P (ISO 15681-2), and total Phosphorous (ISO 15681-2), analyzed by Eurofins Environment Testing Norway, Bergen, Norway. Microbial biomass concentrations were determined by epifluorescence microcopy analyses of samples stained by the nucleic acid stain 4⁰,6-diamidino-2-phenylindol (Porter and Feig, 1980).

### 2.5. Calculations and statistics

Non-linear regression analyses were performed by a 1st order rate approach with determination of lag-phases included using the option "plateau followed by one-phase decay" in GraphPad Prism vs. 6.0 (GraphPad Software Inc., La Jolla, CA, USA). Rate coefficients (k1) were determined for the decay-period, the plateau period defined the lag-phase, and half-lives were determined from rate coefficients and plateau periods (t1/2 = plateau period + 0.693/k1). Rate data were determined for both single oil components and for 22 oil compound groups described in the Oil-Spill Contingency and Response model OSCAR (Reed et al., 2000). The group composition is described in Table S1.

Column statistics were compared by Wilcoxon matched paired test in GraphPad Prism vs. 6.

## 3. Results and discussion

### 3.1. Generation and maintenance of oil dispersions over time

Dispersions of Macondo oil mixed with Corexit 9500A (DOR of 1:100) were generated by different seawater flow-rates through the oil droplet generator system, from 50 to 150 ml/min. This resulted in oil dispersions with median droplet size distributions of approximately 10 l m to 30 l m in diameter (Fig. 1). The oil pump of the dispersion generator was set to generate fixed nominal oil concentrations during the dispersion generation (0.2–200 mg oil per L of water), and good agreement between nominal oil concentrations and measured oil droplet concentrations was recorded (data not shown). Recent studies have shown that nearly the same oil droplet size distribution is generated in this system both with and without premixing of oil with chemical dispersant (Nordtug et al., 2011).

The carousel system was developed for maintaining the droplet size distribution in the oil dispersions while incubating the dispersions over time. All experiments in the carousels were conducted in air-tight flasks without headspace to avoid evaporative depletion. The system was able to handle dispersions of fresh Macondo oil with small droplets, in the diameter size range of 10–30 l m, with rising velocities of 1.6–14.4 cm/h, according to Stoke's law. We believe the ability of keeping the droplets in suspension is due to the combined effect of the turbulence created in the flasks and the fact that the oil droplet rising velocities will make them constantly change direction in relation to any fixed point at the flasks inner surface. Larger than 30 l m oil droplets resulted in inhomogeneous dispersions during transfer from dispersion generator to flasks in carousel system because of elevated rising velocities. In initial experiments with 10 l m median volumetric droplet dispersions in a sterilized system (filtered seawater poisoned with $HgCl_2$), the droplet sizes were maintained for at least 28 days in the carousel system, while measured droplet concentration decreased (see Supplementary Information, Fig. S1).

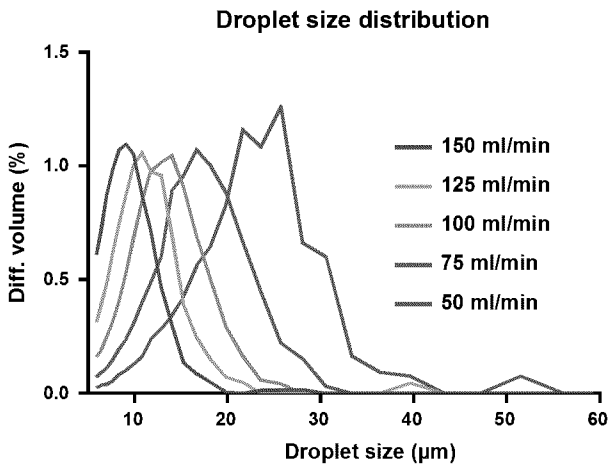


Fig. 1. Average oil droplet size distributions generated in the oil dispersion generator at different seawater flow-rates after premixing of the oil with Corexit 9500A.

### 3.2. Biodegradation experiment with two dispersions of different oil droplet size distributions

An oil dispersion biodegradation experiment was performed at 5 fC (64 days) with nominal oil concentrations of 2 mg/L generated in the dispersion generator at median oil droplet sizes on volume of 10 l m and 30 l m in diameter, and with natural seawater pre-adapted to the oil and temperature (see Section 2). The low oil concentration used in this experiment is consistent with recent recommendations to avoid too high oil loading during biodegradation studies of dispersed oil (Lee et al., 2013). Seawater pre-adaption was included since many offshore oil production areas may be exposed to hydrocarbons through natural seepage or produced water releases. For instance, a recent hydrocarbon seepage flux of 2.2–18 ┐ $10^7$ tons per year has been estimated for the GoM region, corresponding to 14–120% of the DWH discharge rate (Smith et al., 2014). Analyses of macronutrients ($NO_3$ + N $O_2$–N, $NH_4$–N and o-$PO_4$–P) and dissolved oxygen showed no apparent limitations in oxygen or inorganic nutrient levels during the biodegradation experiment (Supplementary Information, Figs. S2 and S3).

#### 3.2.1. Oil droplet sizes and concentrations

The oil droplet size distributions and concentrations were followed in the dispersions during the biodegradation experiment (Fig. 2). Results from Coulter Counter analyses showed that the initial median oil droplet size distributions in the 10 l m and 30 l m dispersions were 11.0 ± 0.04 l m and 29.4 ± 3.5 l m, and that the 10 l m and 30 l m dispersions represented oil surfaces of 10.9 ± 0.2 ┐ $10^5$ and 5.4 ± 0.9 ┐ $10^5$ l $m^2$/ml, respectively. The dispersions with the smaller droplets therefore contained approximately twice the surface area of the dispersions with the larger droplet. Assuming a microbial size of 1 l m in diameter and the maximum microbial density of 1 cell/l $m^2$ of oil droplet surface area (Horowitz et al., 1975; Vilcaez et al., 2013) the initial oil droplet concentrations represented sufficient surface areas for colonization of up 10 ┐ $10^5$ cells/ml in the 10 l m dispersions and 5 ┐ $10^5$ cells/ml in the 30 l m dispersions. Initial cell concentrations determined by epifluorescence microscopy were 8 ┐ $10^5$ and 12 ┐ $10^5$ cells/ml in the 10 l m and 30 l m dispersions, respectively. The oil droplets therefore represented surface areas for attachment of the entire bacterial population in the 10 l m dispersions and approximately 40% of the population in the 30 l m dispersions at the start of the experiment.

The oil droplet size distributions during the biodegradation period (Fig. 2A) were maintained in the 10 l m dispersions (average median droplet size of 3 replicates ranging from 10.7 to 13.4 l m in the natural unfiltered seawater and 8.5–11.1 l m in sterile dispersions). However, the 30 l m dispersions in natural

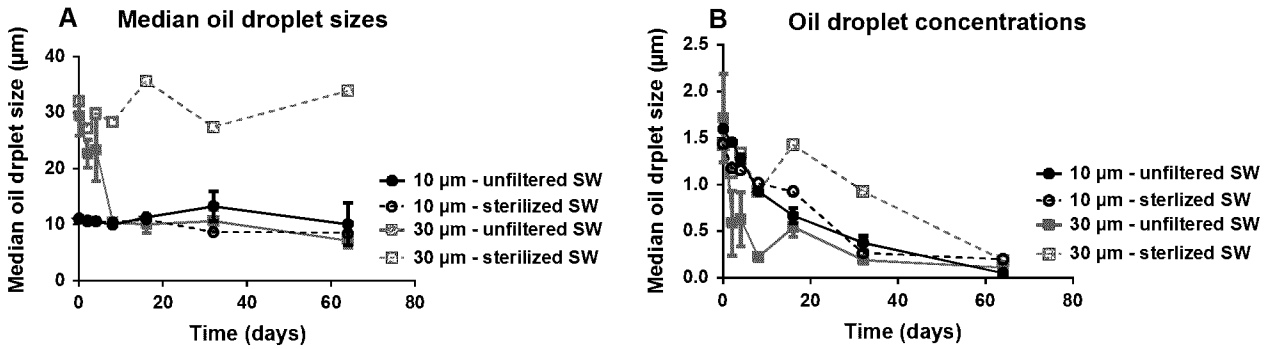


Fig. 2. Median oil droplet sizes (A) and concentrations (B) in oil dispersions generated during a biodegradation period of 64 days at 5 fC in natural unfiltered seawater (unfiltered SW), or in filtered (0.1 l m) and sterilized ($HgCl_2$) seawater (sterilized SW). The dispersions were generated at nominal particle sizes of 10 and 30 l m diameter. The dispersions in unfiltered seawater were analyzed in triplicate (error bars show standard deviation), while sterile samples were analyzed as single samples.

seawater experienced a rapid decline in droplet size between days 0 and 8, from 29.4 to 10.4 l m in average diameter (3 replicates), with a subsequent particle size between 10.2 and 13.4 l m median in the period from day 8 to 64. In contrast, the median oil droplet diameter was maintained in the sterile 30 l m dispersions, ranging from 27.2 to 34.9 l m during the experimental period (Fig. 2A). When oil droplet concentrations were determined by Coulter Counter analyses the concentrations declined more rapidly in natural unfiltered seawater than in the sterilized dispersions. In the 10 l m dispersions the concentrations were decreased from days 0 to 8 by 41.9% (from 1.60 to 0.93 mg/L average values) in natural unfiltered seawater and by 29.2% (from 1.44 to 1.02 mg/L) in the sterilized dispersions, while the reductions in the 30 l m dispersions were 86.9% (from 1.72 mg/L to 0.22 mg/L) and 35.0% (from 1.43 mg/L to 0.93 mg/L) in unfiltered and sterilized seawater, respectively (Fig. 2B). In the sterilized systems with 30 l m oil droplets it was evident that the larger droplets were removed faster than the smaller droplets (Supplementary Information, Fig. S4D). Reduced concentrations of droplets may therefore be caused by removal of the larger droplets with the fastest rising velocities or by droplet coalescence, generating droplets of sizes outside the measuring range of the Coulter Counter instrument (5.6–100 l m), as shown in oil droplet coalescence models (Sterling et al., 2004). The 10 l m dispersions also included oil droplets smaller than the lower instrumental measuring size of 5.6 l m (Supplementary Information, Figs. S4A and S4B). In addition, oil droplets could be removed from the system by attachment to the glass walls of the flasks, as measured by chemical analyses (see below). The higher reduction in oil droplet concentrations in unfiltered than sterilized dispersions may be caused by integration of droplets in "clusters" or "flocs" in natural seawater, which were visually observed in the experiment. These aggregates have been observed in several biodegradation studies of dispersed oil (e.g. Swannell et al., 1997; Harris et al., 2002; MacNaughton et al., 2003; Bælum et al., 2012).

### 3.2.2. Biodegradation of targeted oil compounds

Concentrations of 183 targeted semivolatile or volatile oil compound measured by GC–MS analyses showed that 81.4% of these were detected in the dispersions above the LOD (0.01 l g/L) at the start of the experiment. Compounds not detected above LOD included $C_0$–$C_4$ phenols and benzothiophenes (Supplementary Information, Fig. S5), while additional 13 compounds (7.1%) with concentrations close to LOD (60.1 l g/L) were excluded for biodegradation determination (Supplementary Information, Fig. S5).

Depletion of semivolatile $nC_{10}$–$nC_{36}$ alkanes and non-alkylated and alkyl-substituted decalines, naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, fluoranthenes and chrysenes were examined in the dispersions after normalization against the persistent biomarker 17a(H),21b(H)-Hopane (30ab Hopane), commonly used in biodegradation studies (Prince et al., 1994; Page et al., 1995; Wang et al., 1998). The depletions were determined as percentages of normalized data at the start of the experiment (day 0) for each target oil compound (Fig. 3). In average, the oil compound groups showed low to negligible depletion in sterilized dispersions during the first 32 days (average <1%), although decaline concentrations were reduced by more than 20%. After 64 days the oil compounds were further depleted in the sterilized dispersions (average reduction of 19%). However, compounds in natural unfiltered seawater were mostly reduced to near completion before they were depleted in the sterilized dispersions. The oil compound depletion in natural unfiltered seawater was therefore mainly the result of biotransformation.

Low-range ($nC_{10}$–$nC_{15}$) and medium-range ($nC_{16}$–$nC_{21}$) molecular weight (MW) n-alkanes were rapidly biotransformed after 4 days in the 10 l m dispersions (76.3 ± 2.7 and 74.5 ± 1.9% depletion, respectively), while biotransformation of these n-alkanes started later in the 30 l m dispersions and did not become evident until 8 days (84.2 ± 4.6 and 82.2 ± 3.4% degradation, respectively) in the 30 l m dispersions (Fig. 3A). Faster biotransformation of the low-range and medium-range MW n-alkanes was therefore measured in the 10 l m than the 30 l m dispersions. Also decaline biotransformation started faster in the smaller droplet dispersions, between days 8 and 16 in 10 l m dispersions (60.6 ± 3.6% degradation), and between days 16 and 32 (88.7 ± 9.5% degradation at 32 days) in the 30 l m dispersions (Fig. 3A). However, high-range MW n-alkanes ($nC_{22}$–$nC_{36}$) shower slower and more similar biotransformation in the two dispersions (73.0 ± 4.8 and 63.5 ± 0.5% degradation in the 10 l m and 30 l m dispersions after 16 days)(Fig. 3A).

Low-range and medium-range MW PAH-compounds (2- to 3-ring PAH) were biotransformed between day 8 and 16 in both dispersions, with 99.7 ± 0.2 and 88.9 ± 9.0% degradation after 16 days in the 10 and 30 l m dispersions, respectively (Fig. 3B). Also for these PAH compounds faster biodegradation in the 10 l m than the 30 l m oil droplet dispersions was indicated. However, larger PAH (4- to 5-ring) were only biotransformed between 32 and 64 days, with 95.7 ± 5.2 and 88.7 ± 2.1% decay in the 10 and 30 l m dispersions after 64 days.

VOC compounds determined by P&T GC–MS analyses could not be normalized against a biomarker, since analyses of these did not include any recalcitrant biomarker. Determination of % concentrations relative to 0-day concentrations for the alkane and aromatic VOC compound groups showed biotransformation mainly between 8 and 16 days, resulting in 99.6 ± 0.05 and 96.5 ± 5.0% depletion of

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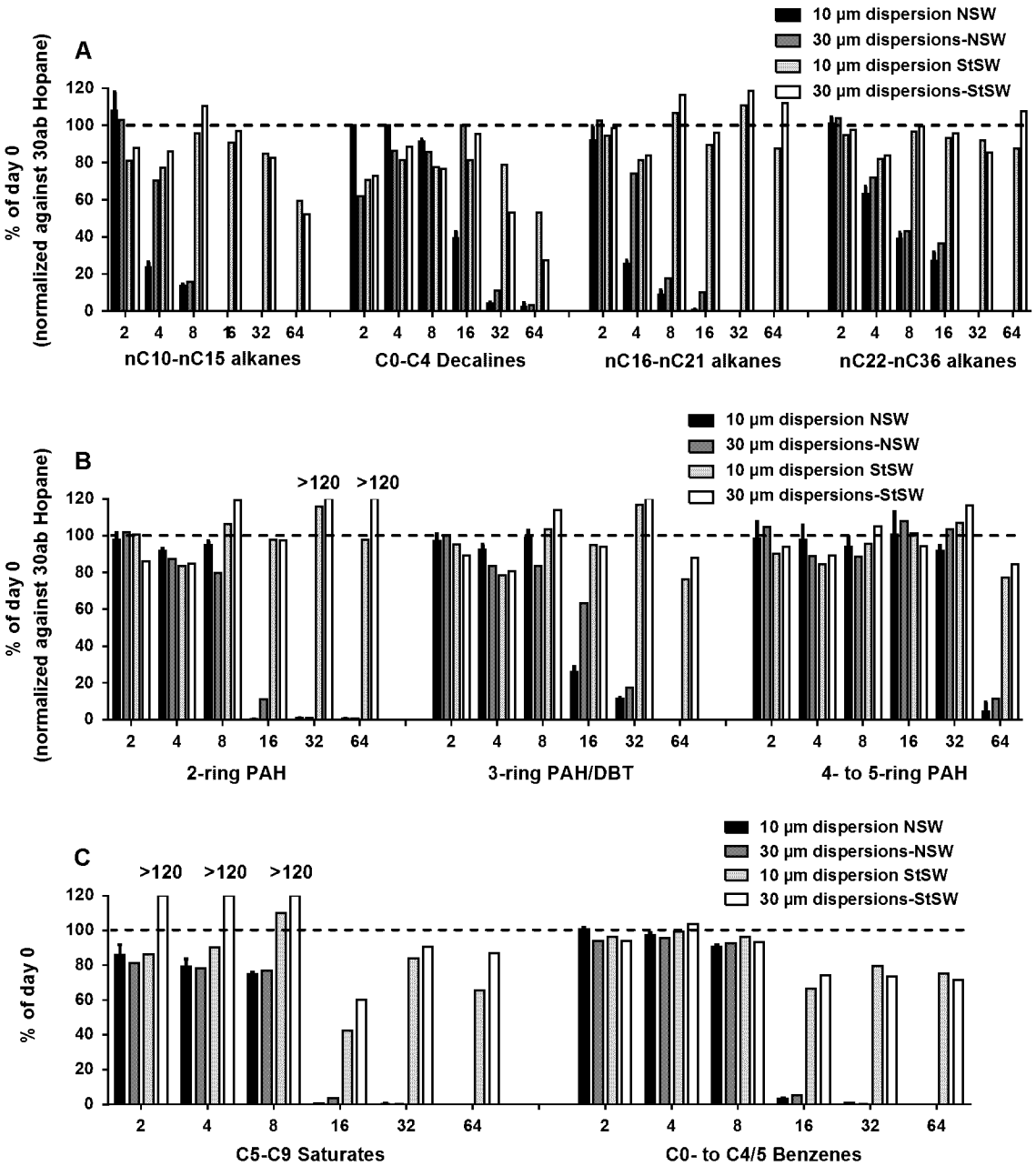


Fig. 3. Percentage concentrations compared to day 0 of semivolatile n-alkanes and $C_0$–$C_4$ alkylated decalines (A), semivolatile 2–5 ring PAH (B), and volatile alkanes and aromatic hydrocarbons (C) in 10 l m and 30 l m dispersions in natural seawater (NSW) and sterilized seawater (StSW) during an incubation period of 64 days, with samples collected after 2, 4, 8, 16, 32 and 64 days. The percentages of semivolatile compounds were determined from GC–MS analyses (triplicate) normalized against the biomarker 30ab Hopane with standard deviation error bars of 3 replicates. Volatile compounds were determined without normalization. The broken line shows the 0-day 100% for each target compound.

$C_5$–$C_9$ alkanes in 10 l m and 30 l m dispersions, respectively, while corresponding data for $C_0$- to $C_4$/$C_5$ benzenes were 96.8 ± 0.5 and 94.4 ± 2.3% depletion (Fig. 3C). Although sterilized dispersions also showed decreased concentrations of volatiles after 16 days (39.7–57.7% and 25.9–33.5% depletion of saturates and benzenes, respectively) most of the depletion in natural unfiltered seawater may therefore be accounted for by biodegradation.

Non-linear regression analyses of single oil compounds (normalized against 30ab Hopane) were performed by 1st order rate kinetics not including the determined lag-phases, and rate coefficients and half-lives for targeted oil compounds were determined in the dispersions. Low oil concentrations with no significant increase in microbial concentrations (epifluorescence microscopy) during the biodegradation period (average cell numbers differed with a factor of 1.02 between days 0 and 64) argued for 1st order kinetics to determine biotransformation coefficients and half-lives (Battersby, 1990). Non-responsive periods (lag-phases) were observed for most of the targeted compounds (Fig. 3). During the DWH spill it was suggested that deepwater with bacteria re-entered the spill site and caused accelerated hydrocarbon biodegradation (Valentine et al., 2012), resulting in a situation in which hydrocarbon-stimulated bacterial populations eventually could degrade oil compounds without a preceding lag-phase.

First-order rate calculations of targeted semivolatile n-alkanes and 2- to 4-ring PAH normalized against 30ab Hopane were performed (Fig. 4, Table S2). Half-lives calculated from the rate

coefficients varied from 0.6–5.6 days (median 1.1 days) and 1.1–11.1 days (median 2.5 days) for $nC_{10}$–$nC_{30}$ alkanes in 10 lm and 30 lm dispersions, respectively, while corresponding data for 2- to 4-ring PAH were 0.9–31.9 (median 5.3 days) and 0.9–54.9 days (median 10.2 days). The half-lives for most of the targeted compounds (44 of 48 compounds) were lower in the 10 lm than the 30 lm dispersions, and the differences between the dispersions were significant ($P < 0.05$; Wilcoxon non-parametric t-test). The n-alkane half-lives were increased with longer carbon-chains in both dispersions, primarily in the high-boiling-point range (P $nC_{21}$). PAH half-lives increased in both dispersions with increasing numbers of aromatic rings and with degree of alkyl-substitution, except for the chrysenes (Fig. 4). Only small differences in half-lives were determined for chrysenes, which appeared in low concentrations in the dispersions (sum of $C_0$–$C_4$ chrysenes of 0.59 and 0.79 lg/L in 10 lm and 30 lm dispersions, respectively; supplementary information Fig. S5). Small oil droplets therefore had a positive impact on biotransformation of both n-alkanes and PAH. In a recent study of Macondo oil biodegradation under a near-surface temperature relevant for the GoM, comparing physically and chemically dispersed oil, we observed higher biodegradation differences related to droplet size for n-alkanes ($nC_{10}$–$nC_{30}$) than 2- to 4-ring PAH (Brakstad et al., 2014). However, in the near-surface oil biodegradation study both temperature (30–32 fC), experimental system and oil droplet size distributions differed from the current experiment. The different temperatures will also stimulate different taxa of oil-degrading bacteria, as shown from field analyses of the DWH incident, in which none of the predominant bacteria in the deepwater plume (Oceanospirillales, Colwellia and Cycloclasticus) were abundant in surface slicks (Redmond and Valentine, 2012). Detailed results from characterization of cell counts and bacterial communities from the current study will be presented in a separate manuscript (Brakstad et al., in preparation). And importantly, the oil characteristics will be different at the two temperatures. For instance some of the larger n-alkanes may generate wax crystals at low temperature, thereby becoming less susceptible to biodegradation.

First-order rates are often calculated without accounting for the lag-phases. In these studies the lag-periods become a part of the half-live determination. In Table S2 (Supplementary Information) the half-lives are also determined as the sum of the lag-periods and the half-lives determined from the rate coefficients. By these calculations the n-alkane half-lives varied from 2–17.6 days in the 10 lm dispersions and 3.1–20.8 days in the 30 lm dispersions. PAH half-lives varied correspondently from 8.8–49.9 and 8.7–79.9 days in the two dispersions. The same trends for n-alkanes and PAH were observed with these half-life calculations as described above, with generally shorter half-lives of the same compounds in the 10 lm than in the 30 lm dispersions. The sums of half-lives and lag-phases also differed significantly between the 10 lm and the 30 lm dispersions ($P < 0.05$; Wilcoxon non-parametric t-test).

Our n-alkane and PAH biodegradation data, using coastal Norwegian seawater from 80 m depth, mainly coincided with results from studies with chemically dispersed oils incubated at low temperature (L 1 to +8 fC), in which n-alkane depletion corresponded to half-lives of 2 to approximately 10 days, while 2- to 4-ring half-lives ranged between 2 and 37 days (Siron et al., 1995; Venosa and Holder, 2007; Prince et al., 2013; McFarlin et al., 2014). Also results from the DWH deepwater plume samples and laboratory studies with microbial consortia or seawater from GoM indicated average n-alkane ($nC_{13}$-$nC_{26}$) half-lives of 1.2–6.1 days (Hazen et al., 2010), showing good agreement with our results. In a recent study with small droplet (10–30 lm) dispersions of Macondo oil in GoM deepwater, biotransformation of 2–3 ring PAH appeared mainly between 9 and 39 days of incubation, while 4–6 ring PAH

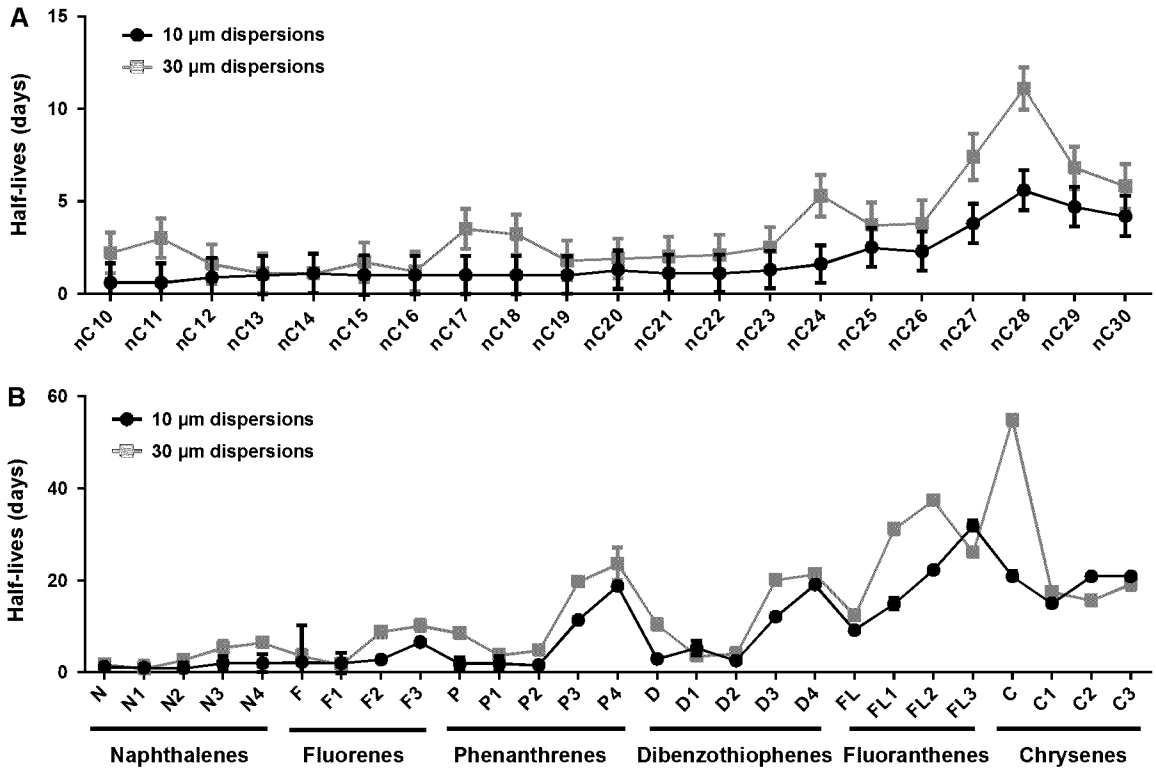


Fig. 4. Half-lives of $nC_{10}$–$nC_{30}$ alkanes (A) and naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, fluoranthenes and chrysenes (B) in 10 lm and 30 lm dispersions with standard deviation errors bars of 3 replicates. Half-lives were determined from rate coefficients without lag-periods included. The numbering of the aromatic groups describes the degree of alkyl-substitution.

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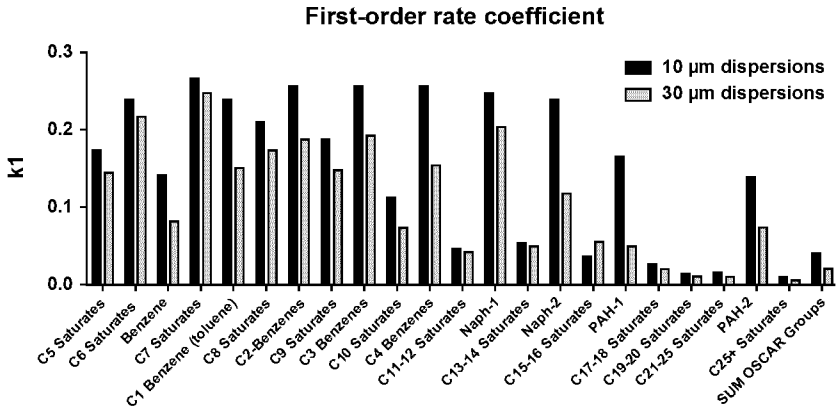


Fig. 5. First-order rate coefficients for oil compound groups of the Macondo oil in 10 and 30 l m dispersions.

transformation had started after 39 days of incubation (Wang et al., 2014), consistent with PAH results from our study.

Oil compound glass wall attachment is well known, and comparison of oil concentrations (TEOC analyses) in water and on glass walls rinsed with solvent (days 0, 8 and 32) showed a gradual increase of wall-attached material, from <3% of total TEOC (day 0), to up to 45% (30 l m dispersions at day 32). Targeted analyses of compounds normalized against 30ab Hopane showed relative preference of 2-ring and non-alkylated 3-ring PAH for the water-phase, while larger alkylated 3-ring and 4- to 5-ring PAH, decalines and n-alkenes gradually distributed between the water- and glass-phase (results not shown). These data emphasize that degradation of dispersed oil in laboratory systems is a result of processes in both water and glass wall surfaces.

### 3.2.3. Biodegradation of oil compound groups

The well-known targeted compounds described above only cover a fraction of the oil. Comparison of TEOC concentrations (GC-FID analyses) with the targeted SVOC and VOC saturate and aromatic oil compound (GC–MS analyses) showed that the sum of the targeted compounds (n-alkenes, 2–5 ring PAH, volatile $C_5$–$C_9$ saturates and $C_0$–$C_5$ benzenes) constituted 33.5% and 40.4% of the sum of TEOC and VOC concentration at the start of the experiment in the 10 l m and 30 l m dispersions, respectively (Supplementary Information, Fig. S6). The TEOC concentrations determined by GC-FID analyses represented 72% and 81% of the oil droplet concentrations measured by the Coulter Counter analyses for the two dispersions, and these results corresponded well with the assumption from true boiling point curves, assuming that $C_5$–$C_{36}$ saturates (boiling points of 27 to approximately 500 fC) represent 70–80% of typical crude oil (Pasquini and Bueno, 2007).

Biotransformation rate coefficients and half-lives of 22 volatile and semivolatile oil compound groups, representing the boiling point range described above (Table S1) were calculated, including $C_5$–$C_{36}$ saturates and 1- to 5-ring aromatic compounds (Reed et al., 2000). The results of Fig. 5 and Table S3 showed rate coefficients of 0.0096–0.2665 (median 0.1692) in the 10 l m dispersions and 0.0054–0.2475 (median 0.0995) in the 30 l m dispersions. These rates resulted in half-lives of 2.8 to 72.2 days (median 4.1 days) and 2.8 to 128.3 days (median 7.2 days) in the 10 and

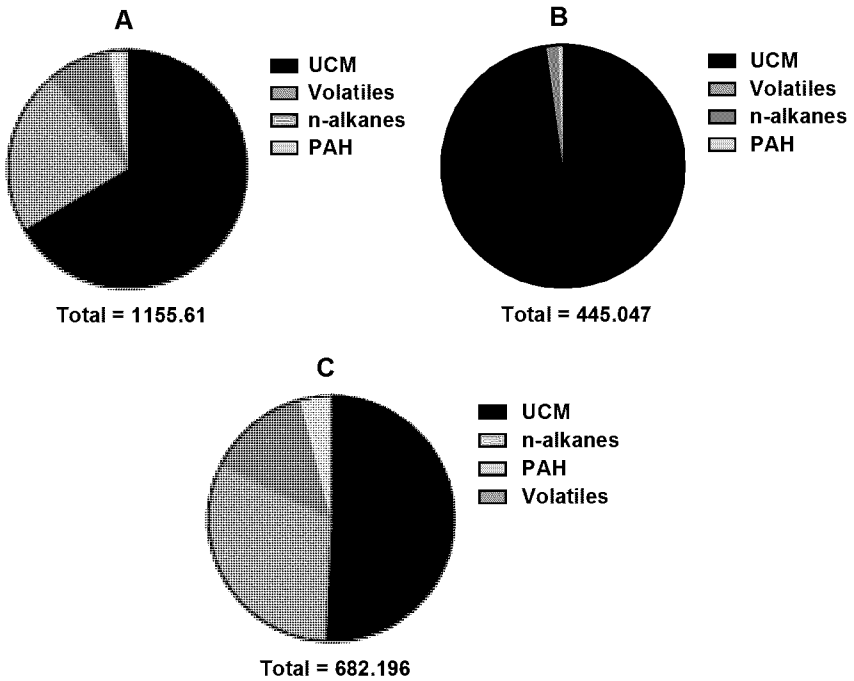


Fig. 6. Distributions of targeted oil compounds and UCM at the start of the biodegradation (A) and after 32 days of incubation in unfiltered (B) and sterilized (C) dispersions. The total concentrations of TEOC (l g/L) are shown below each pie chart.

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30 l m dispersions, respectively. The rate coefficients were higher in the 10 l m than the 30 l m dispersions for all oil compounds, except for $C_{15}$–$C_{16}$ saturates. Comparison of the rate coefficients in the two dispersions showed significant differences ($P < 0.05$; Wilcoxon non-parametric t-test). The rate coefficients were higher in favor of the 10 l m dispersions by factors of 1.21 and 1.67 (median values) for the saturate and aromatic compound groups, respectively. The rate coefficients were generally higher for the aromatic (average of 0.175039) than the saturate (0.099304) oil compound groups when data from both dispersions were compiled. This is probably associated with the water-solubility of the aromatic hydrocarbons, as well as the presence of poorly biodegradable branched and cyclic alkanes in the semivolatile saturate groups.

In previous studies we have compared dissolution and biodegradation of oil compounds from thin oil films (10–20 l m thickness) immobilized on hydrophobic adsorbents, showing that fast dissolution of naphthalenes and non-alkylated 3-ring PAH resulted in biodegradation mainly of dissolved compounds, while negligible dissolution of n-alkanes ($nC_{12}$–$nC_{36}$) resulted in biodegradation of these compounds exclusively on the oil–water interphases. For the larger PAH-compounds dissolution decreased with increasing numbers of aromatic rings and alkyl substitution, with biodegradation of these both as dissolved and as oil-associated compounds (Brakstad et al., 2004; Brakstad and Bonaunet, 2006). Oil compound biodegradation is therefore a complex process, involving bacterial communities in the water-phases as well as bacteria attaching the oil surfaces.

The rate for the sum of the 22 oil compound groups in this study was also faster in the 10 l m ($k1 = 0.03984$) than the 30 l m ($k1 = 0.02004$) dispersions, resulting in half-lives of 17.4 and 34.6 days in the two dispersions (Fig. 5; Table S3). Since the sum of these groups may represent most of the oil, these numbers may be used as biotransformation rates for the oil. The oil droplet size was therefore important both for the biotransformation rates of the oil compound groups and the sum of these groups used in this study and presenting a boiling point range of 27–>500 fC.

The saturates representing the $C_{10}$ to $C_{25+}$ oil compound groups are mostly unidentifiable oil compounds, often termed as the unresolved complex mixture (UCM) (Gough and Rowland, 1990; Killops and Al-Juboori, 1990), and accounts for 60–70% of the groups. Comparison of the sum of TEOC and VOC concentrations with targeted compound groups of n-alkanes, PAH and volatile hydrocarbons showed that the UCM became the predominant oil fraction during the biodegradation period (Fig. 6; Fig. S6, Supplementary Information). Several studies have shown that the UCM fraction includes compounds that are not readily susceptible to biodegradation (Reddy et al., 2002; Booth et al., 2007). The UCM was predominant in each of the saturate groups from $C_{11}$–$C_{12}$ to $C_{25+}$ (Table S1). The degradation of these compounds decreased by increasing boiling point ranges in both 10 l m and 30 l m dispersions (Table S3), and the rate calculations showed that their degradation was mainly faster in the 10 l m than the 30 l m dispersions (Fig. 5; Table S3).

The result from the current study show that reduced oil droplet sizes resulted in increased biodegradation rates. The use of chemical dispersants will generate small droplet oil dispersions, and the result from this and other studies (e.g. Siron et al., 1995; Venosa and Holder, 2007.; Prince et al., 2013; McFarlin et al., 2014; Brakstad et al., 2014) demonstrate that the use of dispersants to generate small droplets will promote biodegradation in seawater at different environmental conditions. Dispersants like Corexit 9500 are considered to have moderate to low acute toxicity (e.g. Mitchell and Holdway, 2000; Judson et al., 2010), and surfactants like alkyl sulfosuccinates may be biodegradable (Garcia et al., 2009; Bælum et al., 2012). The positive influence of chemical dispersants on the biodegradation of potentially toxic oil compounds may therefore compensate for possible negative effects of dispersant components in the marine environment.

Operationally, dispersants have mainly been used for surface oil spills to remove the slick from the seawater surface by generation of small droplet dispersions in the water column. We have previously shown that oil compounds in surface oil emulsions are poorly biodegradable compared to chemically dispersed oil (Brakstad et al., 2014). The dispersant application during the DWH incident aimed at reducing surface slick generation and may also have contributed to the generation of the small oil droplets in the Macondo deepwater plume. If deepwater injection of dispersant during an oil spill is able to reduce oil droplet size and avoid oil surfacing, this may enhance oil compound biodegradation and thereby additionally reduce the impacts of the spill. However, it is important to emphasize the lack of knowledge related to the many unidentifiable oil compounds, both with respect to biodegradability and toxic effects.

Although the water used in the current study was Norwegian coastal seawater, the results may be related to the Macondo deepwater plume. Both oil, oil droplet size distribution (North et al., 2011) and seawater temperature was similar in the current experiment and the DWH deepwater plume. Our experiments were performed at atmospheric pressure, but laboratory experimental studies have shown that bacteria associated with deepwater plume biodegradation of the Macondo oil also biodegraded the oil at atmospheric pressure (Hazen et al., 2010; Bælum et al., 2012).

## 4. Conclusions

The study presented here compares, for the first time to our knowledge, biodegradation rates in oil dispersions with pre-defined droplet sizes, and under temperatures relevant for a deepwater discharge. The results of this study showed that biodegradation of alkane and aromatic hydrocarbons in a dispersible oil (Macondo) was faster in 10 l m than 30 l m dispersions for targeted oil compounds and oil compound groups, as well as the sum of the groups representing most of the oil. These data indicate that dispersant treatment of deepwater oil spills will be beneficial for the oil compound biodegradation, if oil droplet sizes are reduced. Our data showed good agreement with results from other biodegradation studies performed with chemically dispersed oil at low seawater temperatures. Although the current study was performed in seawater from a Norwegian fjord and under atmospheric pressure, these data may also have relevance for the DWH deepwater oil plume. We used the same oil, similar temperatures (4–5 fC), and oil droplet size distributions were comparable to the DWH deepwater plume. Published oil compound degradation data with GoM seawater or enrichment cultures also showed agreement with our results. Comparison of fate model predictions, laboratory results and field data may further substantiate the fate of oil dispersions in deepwater spills and improve the information concerning the impacted deepwater area of a spill. This information is important to include in risk assessment analyses.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.marpolbul.2015.02.006.

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# Large-scale cold water dispersant effectiveness experiments with Alaskan crude oils and Corexit 9500 and 9527 dispersants

Randy C. Belore [a,*], Ken Trudel [a], Joseph V. Mullin [b,1], Alan Guarino [c,2]

[a] S.L. Ross Environmental Research Ltd., 200-717 Belfast Road, Ottawa, ON, Canada K1G 0Z4
[b] U.S. Minerals Management Service, Engineering and Research Branch, 381 Elden Street, Mail Stop-4021, Herndon, Virginia 20170-4817, USA
[c] MAR Inc., P.O. Box 473, Atlantic Highland, New Jersey 07716, USA

a r t i c l e i n f o

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a b s t r a c t

There continues to be reluctance in some jurisdictions to use chemical dispersants as a viable countermeasure for accidental oil spills. One argument used by some opponents to dispersant use is that "chemical dispersants do not work effectively in cold water". To address this issue, the U.S. Minerals Management Service (MMS) funded and conducted two series of large-scale dispersant experiments in very cold water at Ohmsett – The National Oil Spill Response Test Facility, located in Leonardo, New Jersey in February–March 2006 and January–March 2007. Alaska North Slope, Endicott, Northstar and Pt. McIntyre crude oils and Corexit 9500 and Corexit 9527 dispersants were used in the two test series. The crude oils were tested both when fresh and after weathering. Results demonstrated that both Corexit 9500 and Corexit 9527 dispersants were 85–99% effective in dispersing the fresh and weathered crude oils tested at cold temperatures. The MMS expects that results from these test series will assist government regulators and responders in making science based decisions on the use of dispersants as a response tool for oil spills in the Arctic.

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## 1. Introduction

Considerable skepticism exists concerning the viability of using chemical dispersants on crude oils spills in very cold-water conditions. There are regional concerns that dispersants may not be effective on spills of Alaskan crude oils in cold water, especially those that could take place in the colder months and that dispersants should not be or cannot be used in these conditions. The general misconception is that cold temperatures inhibit dispersant effectiveness (DE). Colder temperatures do increase the viscosity of the spilled oil and dispersant product. Dispersants have been formulated to be relatively non-viscous in cold temperatures and can be successfully applied in cold weather. The viscosity of spilled oil will be higher at low temperature, but possibly not too high for effective chemical dispersion.

A number of bench-scale test programs that investigated the effect of cold temperatures on chemical dispersant effectiveness were completed in the 1980s. Tests completed by Harris and Wells (1980) and Mackay et al. (1980) both showed reduced dispersant effectiveness with colder temperatures. Cox et al. (1981) used similar test apparatus and methods and found that cold dispersant applied to warm oil-water systems worked better than warm dispersant and concluded that dispersants could be effective in cold arctic environments. MacKay and Hassain (1982) studied interfacial tensions in dispersant-oil-sea water systems using a spinning drop technique and found that oil-water interfacial tensions were higher in cold-water thus suggesting that dispersants might be less effective in cold conditions. However, Mackay also stated that the overall effect of temperature on DE would be very complex due to dispersant-oil mixing and interfacial tension modification processes as well as oil viscosity issues. Farmwald and Nelson (1982) conducted tests using cold air (4 to ffi40 ffC) over 1 ffC water and DE was not impaired even at the lowest temperature. He concluded that low air temperature should not govern the decision to use dispersants. The results from bench-scale tests conducted by Byford (1982), Byford et al. (1983) suggested that the optimization of a dispersant formulation for one crude oil at low temperature may not result in optimal results for another crude. Byford also suggested that higher oil viscosities due to cold temperatures might reduce oil re-coalescence of dispersed oil drops and the higher density of the oil reduces buoyancy; both factors resulting in better dispersion with cold temperatures. Cold temperatures did not significantly reduce DE in these tests. He found poor

* Corresponding author. Tel.: +1 613 232 1564.
E-mail addresses: Randy@slross.com, rbelore@storm.ca (R.C. Belore), Ken@slross.com (K. Trudel), joseph.mullin@mms.gov (J.V. Mullin), aguarino@ohmsettnj.com (A. Guarino).
[1] +1 703 787 1556.
[2] +1 732 866 7183.

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correlation between different test apparatus and attributed the differences in results to different mixing energies used in each apparatus. Lehtinen and Vesala (1984) tested DE at various salinities and temperatures and found reduced effectiveness at low salinities and low temperatures. Mackay et al. (1985) proposed mechanisms for chemical dispersion of oil slicks, based on results from bench scale testing and observations, and concluded that chemical dispersion under cold marine conditions is only marginally more difficult or requires only marginally more dispersant unless there is a marked increase in the oil viscosity because the temperature is less than the oil's pour point. Brandvik et al. (1992) achieved 10–90% DE in small-scale tests at 0 °C for a range of dispersants on various weathered oil and water-in-oil emulsions.

Tests were conducted in a large outdoor wave tank, in cold-water conditions (1–13 °C), by Esso Resources Canada (Brown et al., 1985 and Brown et al., 1986). The tests showed that dispersants could be effective in cold conditions under breaking waves (1%–77% DE) and to a lesser extent (3%–33% DE) in non-breaking waves of 10–20 cm in height. The DE estimates were based on extensive in-water oil concentration measurements taken 20 h after the wave action was terminated. The authors noted that the DE measurements under-estimated likely field effectiveness since the waves were not left on during the 20 h prior to measurement and some oil drops rose to the surface under these quiescent conditions whereas they would remain in the water column in the presence of normal turbulence in typical field conditions. Mackay (1995) completed cold-water (4 °C) dispersant effectiveness tests in both a bench scale apparatus (EXDET test) and in the ESSO Resources Canada outdoor test basin using Alaska North Slope Crude oil and Corexit 9527. The bench scale results showed a slight decrease (from 90% to 80%) in effectiveness as the temperature increased from 4 °C to 15 °C suggesting that the cold conditions slightly improved the dispersant performance. The tests completed in the outdoor basin resulted in measured DE values between 80 and 97% for weathered ANS crude oil subjected to breaking waves immediately after the application of dispersant.

In summary, various small- and large-scale DE tests have been completed at cold temperatures in the past with somewhat mixed results. Generally, the results have indicated that chemical dispersants can be effective in cold conditions, but several factors might reduce their effectiveness in the cold.

The goal of this research was to determine if typical Alaskan crude oils are amenable to chemical dispersion in near-freezing temperatures. Large-scale experiments that simulate at-sea conditions were conducted to eliminate the concerns posed when extrapolating laboratory test results to offshore conditions. The mixing energies generated by surface waves in the large tank more closely simulate offshore mixing conditions when compared to bench-scale test systems and full-scale dispersant application equipment can be used to apply the dispersant to realistic slicks. The National Research Council (NRC) strongly supported the use of wave-tank testing in their recent review of chemical dispersants as evidenced in the following quote from the report "... wave-tank tests are an important tool that can be used to tie the artificialities of laboratory studies to the operational realities of dispersant use in spill response" (NRC, 2005).

The DE test series were conducted at Ohmsett – The National Oil Spill Response Test Facility, located in Leonardo, New Jersey, USA. More information regarding the capabilities of this research facility can be found at http://www.ohmsett.com. Twenty-five large-scale dispersant effectiveness experiments were completed in the winter of 2006 using Corexit 9527 (SL Ross, 2006b), the dispersant product presently stockpiled in Alaska. Twenty-one large-scale tests were conducted in the winter of 2007 using Corexit 9500 (SL Ross, 2007), the dispersant that would most likely be used to replace the Corexit 9527 stockpiles if they were depleted. Alaska North Slope, Endicott, Northstar and Point McIntyre crude oils were used in both test programs. Detailed project reports for these two research projects can be acquired from the Minerals Management Services web site (http://www.mms.gov/taprhome/).

## 2. Methods

### 2.1. Overview of test procedure

A test is conducted by laying down a uniform slick of a known quantity of oil on the surface of the Ohmsett tank, spraying the oil with dispersant at a pre-determined dose, subjecting the oil to wave action (breaking waves) for 30 min and then collecting the oil remaining on the surface at the end of the mixing period. The oil discharge and dispersant spraying operations are completed from opposite sides of a moving bridge in a single-pass operation.

A comparison of the oil collected with the oil released provides an estimate of the effectiveness of the dispersant. Control tests are conducted without the application of dispersant to determine potential oil losses by processes other than chemical dispersion, such as sidewall adhesion, evaporation and natural dispersion/dissolution. Dispersant effectiveness (DE) estimates are compared to the oil losses in the control tests to determine if the application of chemical dispersant has a significant or only marginal impact on the survival of the surface oil.

Time is provided between tests (usually between 1.5 and 2 h) to allow large oil drops from a previous test to surface prior to completion of the next test. Immediately before each test, the test area was cleared of oil on the water surface, tank sidewalls and end booms by sweeping it down the tank using the spray from fire nozzles and out of the test area. It has been determined that the dispersant in the water from a previous test has no effect on the outcome of a subsequent test unless the dispersant concentration in the water is greater than about 400 ppm (SL Ross, 2000a). Dispersant concentrations in the tank never exceeded 10 ppm in either of the test programs. The test procedure has been developed over a period of several years and has been refined from the experiences gained from several earlier dispersant effectiveness test projects (SL Ross, 2000a,b, 2002a,b, 2003a,b, 2004a, 2006a) and the National Research Council (NRC) review comments (NRC, 2005).

Ideally, oil in the water column (both particulate and dissolved), on the water surface, on tanks side walls and booms and the amount of oil evaporated should be measured to permit the determination of a mass balance of oil before and after each test to be certain that all of the oil has been accurately accounted for. Unfortunately, completing the measurements necessary to arrive at oil mass balance determinations is not a feasible option in a test of this size. The primary difficulty is in accurately determining the quantity of oil present in the water column during or immediately after a test. The spatial and temporal variability of the dispersed oil in the water column makes it virtually impossible to accurately measure the amount of oil in the water column at a point in time. The number of sensors or sampling points needed to measure the oil concentrations at a sufficient resolution to confidently establish the amount of oil in the water column is economically and logistically unmanageable. This difficulty in measuring the in-water oil present in large-scale test facilities or offshore experiments has been well documented by other researchers (Brown et al., 1987; Goodman, 2004). Goodman stated that "at any scale greater than the size of laboratory apparatus the measurement of mass balance is truly a myth using existing technologies". Bonner (Bonner et al., 2003) attempted

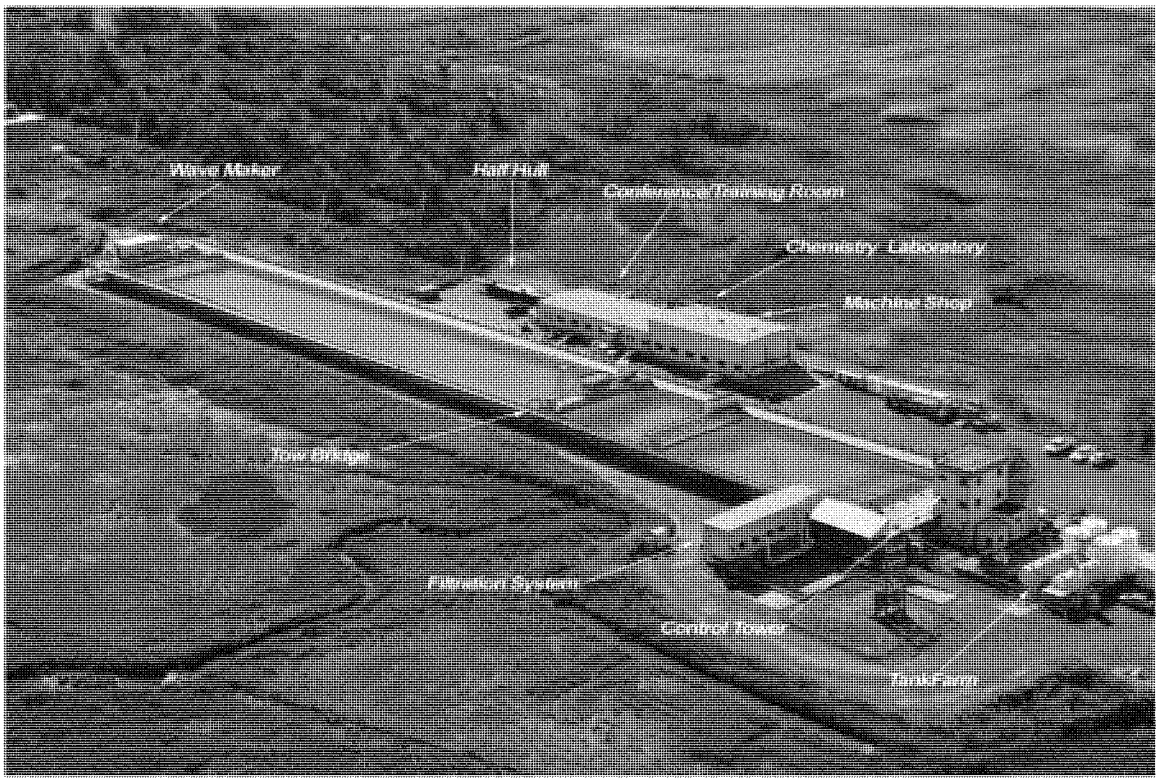


Fig. 1. Ohmsett – the National Oil Spill Response Test Facility.

to achieve a mass-balance measurement in a meso-scale dispersant effectiveness test without success. Depending on the instrumentation used to measure in-water oil quantities up to 30% of the oil was un-accounted for. Only one test was completed in this study, presumably due to the high cost associated with attempting to achieve a mass-balance on the oil.

## 2.2. Major test equipment components

The key component of the test facility is the outdoor, above ground, concrete test tank, seen in Fig. 1, which measures 203 meters long by 20 m wide, by 3.3 m deep. The tank is filled with 9.8 million liters of clear saltwater, is maintained at oceanic salinity (32–35 ppt) and is filtered and treated to maintain water clarity. Ocean waves are simulated with a wave generating system and a wave dampening artificial beach. The wave paddle was operated with a stroke of 7.6 cm (three inches) and a frequency of 35 rpm for these experiments. This wave setting generates significant wave heights (H1/3) of 20–50 cm over the surface of the tank (Asher, 2005) with wave periods between 1.8 and 2.2 s.

The main moveable bridge spans the width of the tank and is used as a platform to discharge the oil and dispersant, to tow oil measuring devices through the dispersed oil clouds and to house personnel and equipment used to monitor the behavior of the spilled oil during an experiment.

The DE experiments are conducted over the full width of the tank and over 150 m of its 203 m length. Containment booms are placed across the tank in front of the wave paddle at the south end and the beaches at the north end to contain the oil during the test and to facilitate collection of oil. Oil was discharged using a progressing cavity pump and a discharge header positioned just above the water surface. Dispersant was applied at 50 psi using a gear pump and Spraying Systems Company flat fan T-jet nozzles (model Nos. 80015 or 8004) mounted on a spray bar positioned approximately one metre above the water surface.

## 2.3. Oil measurement

### 2.3.1. Surface oil

The quantity of oil discharged was determined by measuring the change in oil depth in the supply tank. After the waves were stopped at the end of each test, the remaining surface oil was herded to a collection point at the end of the tank using local currents induced by the spray from fire monitors and skimmed from the surface. The oil and water mixture collected was decanted to remove excess water and the remaining emulsion was analysed for water content to determine the amount of oil collected at the end of the test. Evaporative losses in the control tests were accounted for by comparing the collected oil densities to density versus percent evaporation curves prepared for the test oils.

### 2.3.2. Dispersed oil

In-water oil concentrations were estimated using three or four different techniques depending on the experiment. The oil concentrations were measured to identify when elevated oil concentrations existed to verify that the chemical dispersants were having an effect and to characterize the drop size distributions of the oil dispersions when they occurred. Various methods were deployed in the two test programs primarily to identify the most appropriate method and equipment package for use in future test programs. A Turner 10AU flow-through fluorometer, a LISST 100 particle size analyzer and a Turner Designs TD500D oil-in-water analyzer were used in all of the 2006 tests and a Wet Labs in-situ fluorometer also was used in a few of the early 2006 test runs. In the 2007 test program, only the LISST 100 and a TD3100 oil-in-water analyzer were deployed for in-water oil characterization. The LISST 100 device, the WET Labs in situ fluorometer and the water pump feeding the Turner 10AU and water grab-sampling ports were all positioned at 1.5 meters below the calm water level in both test programs. Technical details for these four oil-in-water measuring systems can be found at the following web sites: http://

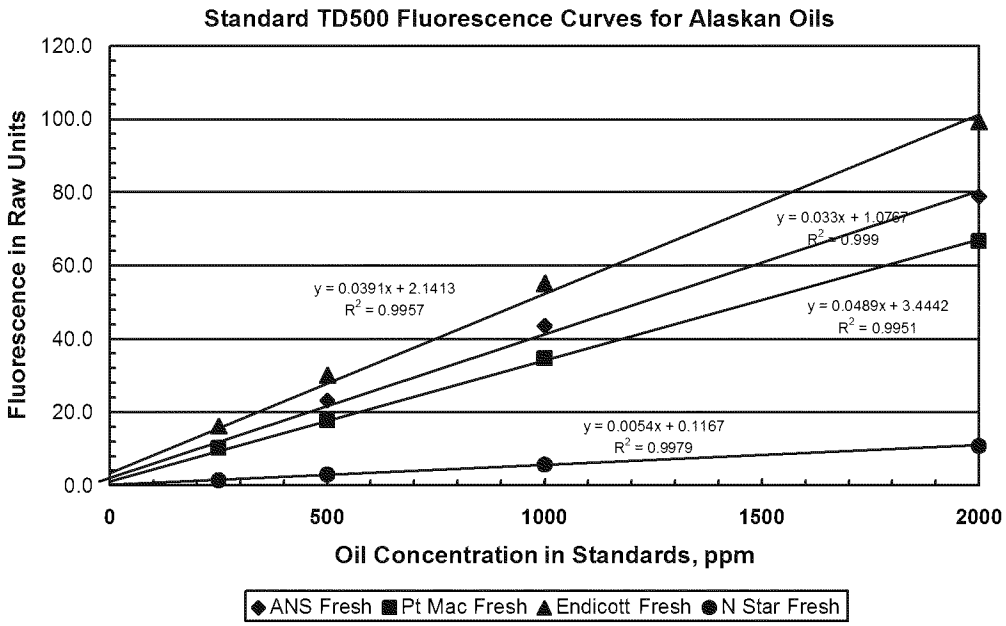


Fig. 2. Standard calibration curves for fresh Alaskan oils using TD500.

www.sequoiasci.com, http://www.oilinwatermonitors.com, http://www.wetlabs.com.

The Turner 10AU flow-through fluorometers were fitted with a 10–046 lamp, a 034–0860 excitation filter (254 nm), a 1/16" attenuator plate and a 10–050R emission filter. The emission filter is broad enough to measure anything from diesel through #6 fuel oil. Prior to the testing the sensitivity and range of the 10AU's were set using standard dispersions of ANS crude oil (pre-mixed with dispersant at a 1:50 dispersant to oil ratio) in salt water. The systems were then calibrated using standard ANS crude and dispersant (pre-mixed 1:50 DOR) dispersions ranging from 10 to 1000 ppm. The 10AU's outputs were regularly checked by injecting them with standard oil-in-water dispersions of 200 ppm. The flow-through cells required periodic cleaning to maintain accurate readings.

The Turner Designs TD500D and TD3100 generate raw fluorescence measurements for solvent (heptane) extracted samples. The raw values are then converted to oil concentration based on calibrations with known oil-in-solvent concentrations. The sensitivity of theses devices were set prior to the test programs to ensure that a linear response to oil concentration in the range of 0–2000 ppm was possible. Calibration curves (see Fig. 2) were established for all of the oils tested. One hundred ml water samples were taken during the experiments and the oil was extracted with 10 ml of heptane. Raw fluorescence measurements from each sample extraction were then converted to oil concentrations using the calibration curves.

The WET Labs in situ fluorometer was used as configured to measure raw fluorescence.

Dispersed oil drop size distributions were measured using the LISST 100 particle size analyzer. The LISST 100 is a laser diffraction device that measures angular scattering distribution in 32 ring detectors corresponding to drop size ranges from 2.5 to 500 l m. The operating status or health of the instrument is checked by recording the background scatter using distilled water. If the scatter matches the factory settings, the glass surfaces are clean and the device is working properly. There are no user adjustments for device calibration only the need to keep the glass surfaces clean during operation. This device also generates an estimate of oil concentration based on the oil drop information gathered.

## 3. Dispersants and oils used in test programs

Corexit 9527 dispersant was used in the 2006 testing and Corexit 9500 was used in 2007.

Four Alaskan crude oils were tested in both 2006 and 2007. They were Alaskan North Slope (ANS), Endicott (End), Pt. McIntyre (PtMc), and Northstar (NS) crude oils. ANS is a blend of crude oils from the various Alaska North Slope fields and is the oil that is exported from Alaska by tankers, whereas the other oils are specific to their Alaskan production areas. In the 2006 test program oils were tested fresh, weathered by removal of light ends using air sparging and weathered by placing the oils on the tank in breaking wave conditions (high-energy 34–35 cpm waves) and non-breaking waves (low-energy 28 cpm waves) long enough for the oil to reach a volume percent loss similar to the air sparged oils. The on-tank weathered oils were weathered on the tank and then collected and stored in drums at 0 fC until used in a test. The oils were weathered, collected and then re-released using the oil discharge header to facilitate the control of the dispersant dosage and to ensure that a similar test method was used in all tests. Only fresh oils and oils weathered by air sparging were used in the 2007 test program.

Air sparging is a standard procedure to weather crude oils that is used by researchers worldwide (SL Ross, 2007). The target evaporative loss for the oils used was 15% by mass for the ANS, Endicott and Pt. McIntrye oils and 30% for the Northstar crude.

One objective of the 2006 testing was to compare the process of on-tank weathering (light-end losses only without significant water-in-oil emulsion formation) to that of air sparged weathering. The goal was not to generate water-in-oil emulsions in the on-tank weathering, but to match the light-end loss achieved in the air sparging process as close as possible. The physical properties of the oils used in the two test programs are shown in Table 1. No oils were weathered "on-tank" in the 2007 test program.

The Endicott oil was not subjected to on-tank weathering in the 2006 program due to time constraints. The on-tank weathered oils formed water-in-oil emulsions of varying water contents and stabilities. Although this was not intended, it was inevitable. The water contents of these oils at the time they were used in the dispersant application testing in the 2006 experiments are shown in Table 1.

Table 1
Physical properties of test oils

| Oil | 2006 Program | | | | 2007 Program | | |
|---|---|---|---|---|---|---|---|
| | Density (mg/l) | Viscosity (cP) 100 s$^{-1}$, 1 ffC | Oil Loss (% Volume) | Water Content (%) | Density (mg/l) @20 ffC | Viscosity (cP) 100 s$^{-1}$, 1 ffC | Oil Loss (% Volume) |
| Alaska north slope | | | | | | | |
| Fresh | 0.863 | 22 | 0 | 0 | 0.862 | 65 | 0 |
| Air sparged | 0.887 | 93 | 15.3 | 0.2 | 0.893 | 200 | 15 |
| Air sparged | – | – | – | – | 0.900 | 300 | 22 |
| On-tank lo-Energy | 0.901 | 203 | 25.1 | 5 | – | – | – |
| On-tank hi-energy | 0.903 | 200 | 26.5 | 16 | – | – | – |
| Endicott | | | | | | | |
| Fresh | 0.9018 | 270 | 0 | 0.2 | 0.901 | 350 | 0 |
| Air sparged | 0.917 | 644 | 20.1 | 0 | 0.916 | 520 | 18 |
| Northstar | | | | | | | |
| Fresh | 0.8025 | 7.6 | 0 | 0 | 0.814 | 6 | 0 |
| Air sparged | 0.839 | 36 | 34.5 | 0 | 0.842 | 30 | 30 |
| On-Tank Lo-Energy | 0.842 | 116 | 37.6 | 40 | – | – | – |
| On-tank hi-energy | 0.843 | 143 | 38.6 | 48 | – | – | – |
| Pt. McIntyre | | | | | | | |
| Fresh | 0.861 | 34 | 0 | 2 | 0.862 | 45 | 0 |
| Air sparged | 0.880 | 76 | 12.5 | 0.5 | 0.898 | 400 | 15 |
| On-tank lo-energy | 0.884 | 214 | 15.9 | 45 | – | – | – |
| On-tank hi-energy | 0.898 | 695 | 27.6 | 48 | – | – | – |

## 4. Test results

### 4.1. Test conditions and raw dispersant effectiveness estimates

The test conditions measured during the experiments (oil viscosities, oil water contents, oil and water temperatures, oil volumes spilled, and dispersant to oil ratios) and estimated Dispersant Effectiveness (DE) without adjustment for control experiment losses are summarized in Tables 2 and 3, respectively.

The "% collected" data in Tables 2 and 3 are the volume percentages of the oil spilled that were collected from the surface after each test (after accounting for water contents in both the discharged and collected oils).

The "% Dispersed/Lost" data are the percentages of oil not accounted for by collection or evaporation estimates. In the "dispersant applied" tests, the "% Dispersed/Lost" estimates were all very high in both the 2006 program that used Corexit 9527 dispersant and the 2007 program that used Corexit 9500. In 2006, there were ten tests with 95% or higher values, four tests with 90% or higher and one test at 85%, with this being the lowest value. In the 2007 program there were nine tests with 95% or higher values and two tests with 90% or higher values.

The "% Dispersed/Lost" values recorded for the control runs (no dispersant applied) in both the 2006 and 2007 programs were generally in the 10 to 25% range meaning that 75–90% of the spilled oil in the control experiments was accounted for by either oil collection or evaporation estimates. The high "% Dispersed/Lost" values in the dispersant applied experiments can thus be confidently attributed to the effect of the applied chemical and not to "natural dispersion" of the oil or adhesion of the oil to tank side walls or booms. Fig. 3 shows a graphical comparison of the "% Dispersed/Lost" results for the dispersant applied and control tests for both the Corexit 9500 (2006 test program) and the Corexit 9527 (2007 test program) results. Due to cost and time constraint inherent in large-scale testing, it was not possible to do replicate testing for the various test combinations that were studied in these test programs. As a result, statistical significance testing on the data results is not possible.

Higher oil losses (38–60%) were encountered in the Northstar control runs than in control runs with all other oils in both 2006 and 2007. This can be attributed to the natural dispersion/dissolution of this very light oil. The reason for the unusually high oil loss recorded for control test #17 for ANS crude oil in the 2007 test program is unknown. The data collected for the control test for the Pt. McIntyre on-tank, high-energy weathered oil in 2006 (test #22) is suspect due to a number of operational difficulties experienced in this test.

There was no difference in the dispersibility of the air sparged versus the on-tank weathered oils in the 2006 test program.

### 4.2. Visual records

All of the experiments were videotaped from the observation tower located on the main bridge. The video was edited to show the progression of the test from the beginning to the end. The complete sets of video summaries for each report are available online at http://www.mms.gov/tarphome.

### 4.3. Dispersed oil concentrations and drop size distributions

Up to four passes were made down the length of the test tank with the main bridge after the oil was discharged to measure in-water oil concentrations and drop size distributions. These measurements were made to confirm the presence of oil in the water column and to characterize the form of the oil (drop size distribution). Graphs of the oil drop size distributions and concentrations recorded in all of the tests are provided in the project reports that can be acquired from the MMS web site referenced earlier. Two examples of these graphs are provided to illustrate the types of measurements that were made during the test programs.

Figs. 4 and 5 show the oil drop size distributions and in-water oil concentration measurements for the 15% air-sparged ANS tests completed in 2007. The "continuous" traces on these plots are from the LISST 100 device that sampled both oil concentration and oil drop size every few seconds as the bridge was moved back and forth dragging the device through the water. The high concentration zones correspond to the times that the LISST sensor was in the dispersed oil cloud. In the control experiment (Fig. 4), elevated oil concentrations (30–50 ppm) were recorded under the slick, but the oil drop sizes in the zones of high oil concentrations were large (volume median diameters (VMDs) or d50's of 250–350 l m). In the dispersant applied case (Fig. 5), the oil drop size distributions were

Table 2
2006 dispersant effectiveness (DE) test conditions and results summary: Corexit 9527 dispersant

| Oil | Initial oil viscosity (cP) | Initial oil water content (%) | Air temp ffC | Water temp ffC | Oil temp ffC | Dispersant temp ffC | Oil volume (liters) | Oil thickness (mm) | DOR | % Collected | % Evaporated | % Dispersed / lost | Test # |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alaska north slope | | | | | | | | | | | | | |
| Fresh | 22 | 0 | ffi2.7 | ffi2 | 7.8 | – | 74.8 | 0.9 | Control | 60.3 | 19.3 | 20.4 | 2 |
| Fresh | 22 | 0 | 1.2 | 0.3 | ffi1.7 | 3.9 | 75.7 | 1.2 | 1:38 | 5.3 | – | 94.7 | 3 |
| Air sparged | 93 | 0.2 | 3.3 | –0.6 | ffi0.6 | – | 75.9 | 1.1 | Control | 77.9 | 9.6 | 12.6 | 5 |
| Air sparged | 93 | 0.2 | 6.2 | 0.0 | 2.2 | 5.0 | 50.4 | 1.1 | 1:26 | 2.7 | – | 97.3 | 6 |
| On-Tank Lo-Energy | 203 | 5 | ffi1.9 | 0.0 | ffi4.4 | ffi1.7 | 69.7 | 2.8 | 1:28 | 2.6 | – | 97.4 | 10 |
| On-tank hi-Energy | 200 | 16 | 0.5 | 0.0 | ffi0.6 | 3.3 | 62.8 | 2.6 | 1:25 | 3.4 | – | 96.6 | 9 |
| On-tank hi-lo Mix | 256 | 14 | 8.6 | 2.8 | 3.3 | 7.2 | 65.2 | 1.2 | 1:21 | 1.1 | – | 98.9 | 23 |
| Endicott | | | | | | | | | | | | | |
| Fresh | 270 | 0.2 | 0.5 | 0.0 | 0.0 | – | 72.5 | 1.2 | Control | 61.8 | 24.7 | 13.5 | 8 |
| Fresh | 245 | 0.2 | 7.1 | 2.8 | 3.3 | 7.2 | 79.8 | 3.3 | 1:27 | 0.4 | – | 99.6 | 17 |
| Air sparged | 772 | 0 | ffi0.7 | 0.0 | ffi1.1 | – | 73.4 | 3.2 | Control | 71.5 | 5.7 | 22.8 | 7 |
| Air sparged | 644 | 0 | ffi0.1 | 0.0 | ffi2.8 | 0.0 | 73.4 | 3.8 | 1:40 | 14.9 | – | 85.1 | 11 |
| Air sparged | 644 | 0 | 15.7 | 3.3 | 10.6 | 13.9 | 77.0 | 2.5 | 1:17 | 8.9 | – | 91.1 | 25 |
| Northstar | | | | | | | | | | | | | |
| Fresh | 7.6 | 0 | 5.6 | 1.7 | 0.0 | – | 80.2 | 1.6 | Control | 31.9 | 45.0 | 23.1 | 13 |
| Fresh | 7.6 | 0 | 7.3 | 1.7 | 2.2 | 9.4 | 69.4 | 1.5 | 1:25 | 3.7 | – | 96.3 | 14 |
| Air sparged | 36 | 0 | 7.3 | 1.9 | ffi1.7 | 0.6 | 75.7 | 3.2 | 1:43 | 8.9 | – | 91.1 | 15 |
| On-Tank Lo-Energy | 116 | 40 | 2.8 | 1.1 | ffi1.7 | – | 47.9 | 1.9 | Control | 49.4 | 12.3 | 38.3 | 12 |
| On-tank hi-energy | 143 | 48 | 1.6 | –2.8 | ffi2.8 | – | 39.9 | 1.7 | Control | 24.2 | 17.2 | 58.6 | 18 |
| On-tank hi-energy | 143 | 48 | 5.6 | 2.2 | 0.0 | 1.7 | 38.3 | 2.4 | 1:23 | 1.7 | – | 98.3 | 16 |
| Pt. McIntyre | | | | | | | | | | | | | |
| Fresh | 34 | 2 | ffi2.0 | 0.0 | 7.8 | – | 66.4 | 2.2 | Control | 76.3 | 12.2 | 11.5 | 1 |
| Fresh | 34 | 2 | 7.6 | 3.3 | 5.0 | 11.7 | 68.4 | 1.1 | 1:18 | 0.7 | – | 99.3 | 21 |
| Air sparged | 76 | 0.5 | 0.6 | –0.4 | ffi0.6 | – | 75.3 | 1.1 | Control | 68.4 | 9.4 | 22.2 | 4 |
| Air sparged | 76 | 0.5 | 5.8 | 2.8 | 2.2 | 8.3 | 67.8 | 2.1 | 1:18 | 0.7 | – | 99.3 | 20 |
| On-tank lo-energy | 214 | 55 | 13.7 | 2.8 | 2.8 | 16.7 | 33.6 | 1.9 | 1:28 | 1.0 | – | 99.0 | 24 |
| On-tank hi-energy | 695 | 48 | 7.8 | 2.8 | 2.2 | – | 28.0 | 0.9 | Control | 19.6 | 3.8 | 76.7 | 22 |
| On-tank hi-energy | 695 | 48 | 3.9 | 2.8 | 0.6 | 4.4 | 39.7 | 3.5 | 1:25 | 5.9 | – | 94.1 | 19 |

Table 3
2007 dispersant effectiveness (DE) test conditions and results summary: Corexit 9500 dispersant

| Oil | Initial oil viscosity (cP) | Air temp ffC | Water temp ffC | Oil temp ffC | Dispersant temp ffC | Oil volume (liters) | Oil thickness (mm) | DOR (Corexit 9500 unless otherwise noted) | % Collected | % Evaporated | % Dispersed / lost | Test # |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alaska north slope | | | | | | | | | | | | |
| Fresh | 65 | ffi6.1 | –4.4 | ffi7.2 | | 80 | 1.06 | Control | 41 | 13 | 46 | 1 |
| Fresh | 65 | 19.2 | 7.2 | 15.6 | 16.7 | 69 | 1.63 | 1:25 | 2 | – | 98 | 19 |
| Air sparged 15% | 200 | ffi2.2 | –4.4 | 0.0 | | 78 | 0.90 | Control | 77 | 5 | 18 | 4 |
| Air sparged 15% | 200 | 0.9 | –3.3 | 0.0 | 12.8 | 77 | 1.04 | 1:17 | 1 | – | 99 | 5 |
| Air sparged 22% | 300 | 14.2 | 5.6 | 13.3 | | 78 | 1.39 | Control | 41 | 8 | 51 | 17 |
| Air sparged 22% | 300 | 14.6 | 5.6 | 13.9 | 15.0 | 71 | 1.46 | 1:24 | 3 | – | 97 | 18 |
| Endicott | | | | | | | | | | | | |
| Fresh | 350 | 1.7 | –2.2 | 1.7 | | 75 | 1.12 | Control | 76 | 5 | 19 | 3 |
| Fresh | 350 | 20.7 | 9.4 | 19.4 | 18.3 | 76 | 1.62 | 1:24 | 2 | – | 98 | 21 |
| Air sparged 18% | 520 | 8.1 | 2.8 | 7.8 | | 76 | 1.59 | Control | 69 | 10 | 24 | 14 |
| Air sparged 18% | 520 | 10.1 | 3.9 | 7.8 | 11.7 | 74 | 1.12 | 18 | 6 | – | 94 | 16 |
| Air sparged 18% | 520 | 12.1 | 4.4 | 11.1 | 10.6 | 71 | 1.38 | 1:21 (C9527) | 7 | – | 93 | 15 |
| Northstar | | | | | | | | | | | | |
| Fresh | 6 | 1.1 | –1.1 | ffi0.6 | | 78 | 0.95 | Control | 52 | 36 | 11 | 9 |
| Fresh | 6 | 3.2 | –0.6 | 3.9 | 10.0 | 78 | 0.97 | 1:18 | 1 | – | 99 | 10 |
| Air sparged 30% | 30 | ffi1.7 | –2.2 | ffi2.2 | | 85 | 1.04 | Control | 49 | 11 | 38 | 6 |
| Air sparged 30% | 30 | 1.1 | –2.8 | ffi0.6 | 10.0 | 77 | 1.15 | v20 | 1 | – | 99 | 7 |
| Air sparged 30% | 30 | 1.7 | –2.2 | ffi0.6 | 8.9 | 73 | 1.15 | 1:19 (C9527) | 1 | – | 99 | 8 |
| Pt. McIntyre | | | | | | | | | | | | |
| Fresh | 45 | ffi1.7 | –4.4 | 1.1 | | 77 | 0.95 | Control | 62 | 15 | 24 | 2 |
| Fresh | 45 | 16.0 | 7.2 | 14.4 | 15.0 | 78 | 1.62 | 1:19 | 1 | – | 99 | 20 |
| Air sparged 15% | 400 | ffi7.7 | –5.0 | ffi3.3 | | 67 | 1.10 | Control | 68 | 9 | 23 | 11 |
| Air sparged 15% | 400 | ffi7.9 | –6.1 | ffi8.3 | 4.4 | 69 | 1.34 | 1:23 | 1 | – | 99 | 12 |

small (d50's less than 25 lm) in the high oil concentration zones (50–150 ppm). Elevated oil concentrations were measured in both the control and dispersant applied tests, but much smaller oil drop sizes were detected in the dispersant applied case. Dispersed oil drops less than 70–100 lm in diameter are generally considered permanently dispersed in a typical offshore environment (Lunel, 1993; Neff, 1990). A theoretical study (Li and Garrett, 1998) of oil drop breakup under typical offshore breaking wave conditions

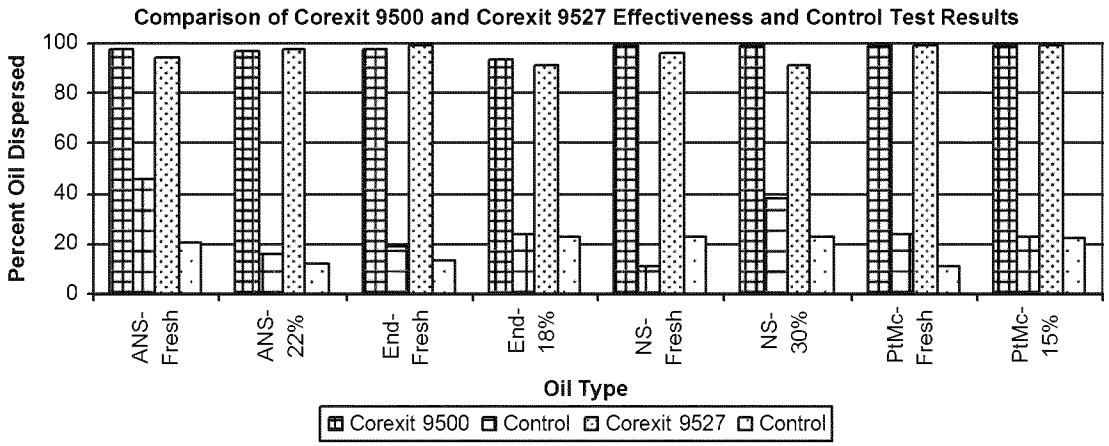


Fig. 3. Comparison of effectiveness results for Corexit 9500 and Corexit 9527.

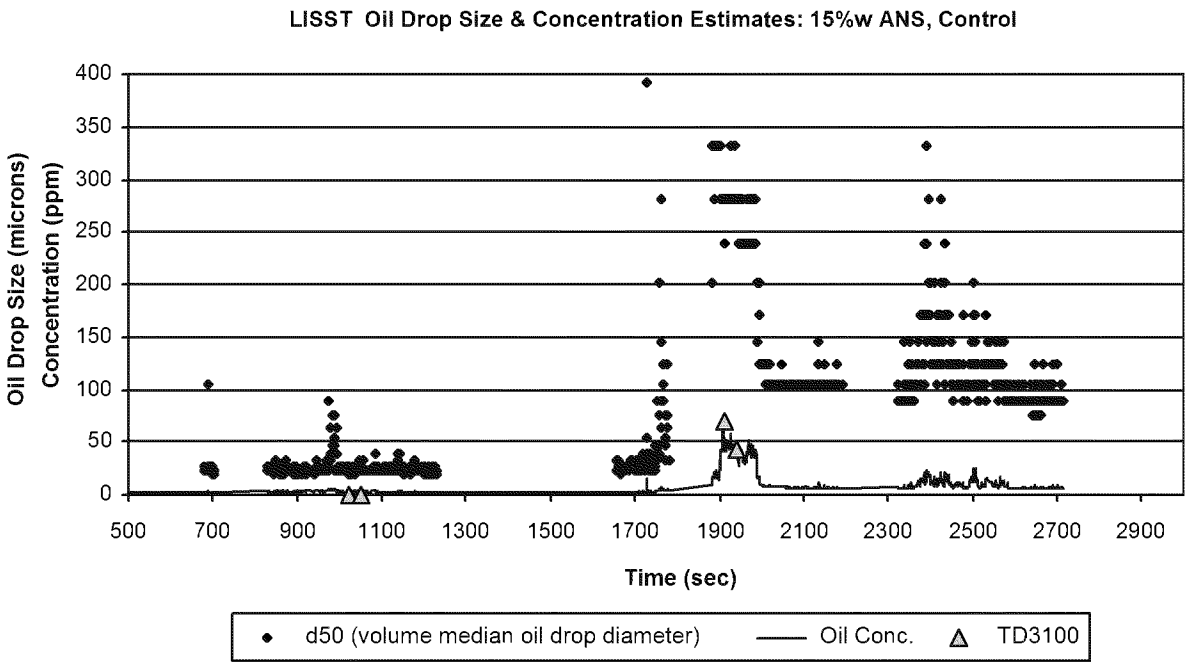


Fig. 4. Oil drop size and oil concentration measurements from a control experiment: no dispersant.

has shown that untreated oil slicks of Prudhoe Bay crude oil will likely be broken into drops between 150 and 1000 l m and treated oil into drops between 10 and 150 l m. These values are supported by the work of Lunel and Neff and are similar to the drop size ranges measured in the control and treated tests in the current study. The drop size results from the control run (Fig. 4) suggest that much of the naturally dispersed oil will not likely be permanently dispersed. The small oil drops recorded in the dispersant applied test (Fig. 5) suggest that the dispersant was effective in generating dispersed oil in small enough drops to be permanently dispersed. The in-water oil characterizations qualitatively support the measurements of oil lost from the surface that are used to determine dispersant effectiveness.

4.3.1. Oil drop size analysis and adjusted DE estimates

The oil drop size data collected for each experiment (described above) has been analysed to determine one) the average VMD drop size, and two) the volume percent of the oil present in the form of oil drops less then 70 l m in diameter. The detailed results of this analysis for both test series are presented in Table 4. The VMD drop size for the control test dispersions were consistently and significantly higher than for the dispersant applied runs in both test programs. The volume of oil present in the water column in the form of drops less than 70 l m in diameter was also much higher in the dispersant tests (70–77%) when compared to the controls (18–34%) in both test series. This would be expected since the role of surfactants in chemical dispersants is to reduce the oil/water interfacial tension and promote the formation of smaller droplets of oil under a given mixing energy. As previously discussed, oil in drops 70 l m in diameter or less were permanently dispersed in offshore dispersant tests (Lunel, 1993; Neff, 1990). These measurements indicate that a high percentage of the dispersed oil in the chemically treated tests in both of these programs would likely remain dispersed in an ocean setting.

The average oil drop VMDs in the control tests of 2006 were consistently smaller than in the 2007 (composite average of 130 l m in 2006 versus 186 l m in 2007: see Table 4) study even though the oil viscosities and temperatures in the two studies were

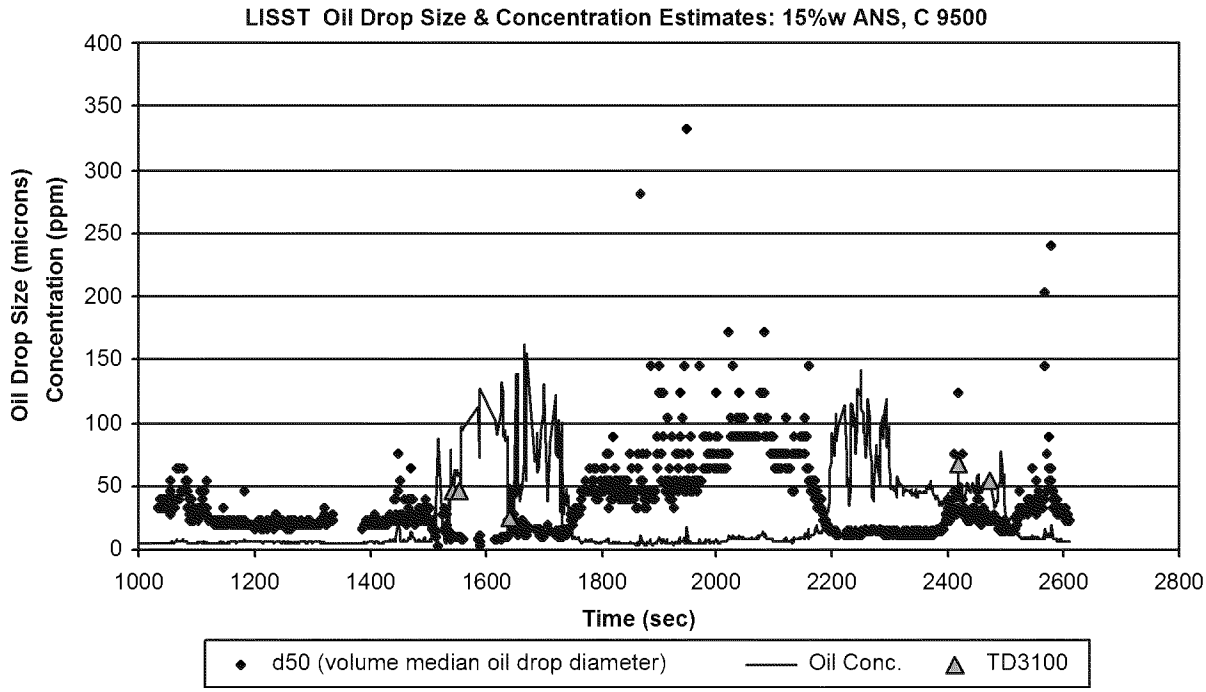


Fig. 5. Oil drop size and oil concentration measurements from a dispersant applied experiment.

similar. This suggests that the energy levels present in the 2006 test program may have been slightly higher than those used in 2007. The oil drop VMDs in the dispersant applied tests were consistently lower in the 2007 tests with Corexit 9500 than in the 2006 test where Corexit 9527 was used (composite average of 35 l m in 2007 versus 50 l m in 2006: Table 4). This, combined with possibly lower energy levels used in 2007, suggests that the Corexit 9500 generated smaller oil drops than Corexit 9527 and was therefore somewhat more effective.

The "volume percent less than 70 micron" values computed for each dispersant applied test and reported in Table 4 have been multiplied by the raw DE values shown in Tables 2 and 3 and Fig. 3 as a method to account for the possible resurfacing of large

Table 4
Oil drop size distribution summaries

| 2006 Test program (Corexit 9527) | | | | 2007 Test program (Corexit 9500) | | | |
|---|---|---|---|---|---|---|---|
| Test # | Test type | Average VMD (l m) | Vol% < 70 (l m) | Test # | Test type | Average VMD (l m) | Vol% < 70 (l m) |
| 1 | Control | 123 | 27.0 | 1 | Control | 176 | 8.1 |
| 2 | Control | 82 | 56.2 | 2 | Control | 198 | 14.5 |
| 4 | Control | 115 | 41.8 | 3 | Control | 173 | 28.9 |
| 5 | Control | 130 | 33.8 | 4 | Control | 151 | 19.0 |
| 7 | Control | 147 | 35.2 | 6 | Control | 225 | 9.7 |
| 8 | Control | 136 | 26.8 | 9 | Control | 166 | 20.3 |
| 12 | Control | 98 | 44.6 | 11 | Control | 249 | 9.2 |
| 13 | Control | 133 | 29.0 | 14 | Control | 209 | 9.8 |
| 18 | Control | 117 | 36.3 | 17 | Control | 125 | 42.8 |
| 22 | Control | 214 | 13.3 | | Averages | 185.8 | 18.0 |
| | Averages | 129.5 | 34.4 | | Std. dev. | 38.4 | 11.5 |
| | Std dev | 35.2 | 11.7 | | | | |
| | | | | 5 | dispersant | 47 | 70.8 |
| | | | | 7 | dispersant | 24 | 83.3 |
| 3 | Dispersant | 80 | 51.8 | 8 | Dispersant | 38 | 77.3 |
| 6 | Dispersant | 23 | 85.9 | 10 | Dispersant | 32 | 79.2 |
| 9 | Dispersant | 80 | 68.6 | 12 | Dispersant | 47 | 67.0 |
| 10 | Dispersant | 42 | 82.4 | 15 | Dispersant | 60 | 64.5 |
| 11 | Dispersant | 43 | 75.8 | 16 | Dispersant | 72 | 58.3 |
| 14 | Dispersant | 73 | 54.8 | 18 | Dispersant | 9 | 91.1 |
| 15 | Dispersant | 46 | 70.6 | 19 | Dispersant | 11 | 86.5 |
| 16 | Dispersant | 74 | 55.4 | 20 | Dispersant | 25 | 82.8 |
| 17 | Dispersant | 24 | 80.9 | 21 | Dispersant | 20 | 89.7 |
| 19 | Dispersant | 76 | 50.7 | | Averages | 35.0 | 77.3 |
| 20 | Dispersant | 18 | 78.5 | | Std. dev. | 20.0 | 10.8 |
| 21 | Dispersant | 17 | 81.1 | | | | |
| 23 | Dispersant | 17 | 81.2 | | | | |
| 24 | Dispersant | 87 | 62.9 | | | | |
| | Averages | 50.0 | 70.0 | | | | |
| | Std dev | 27.3 | 12.7 | | | | |

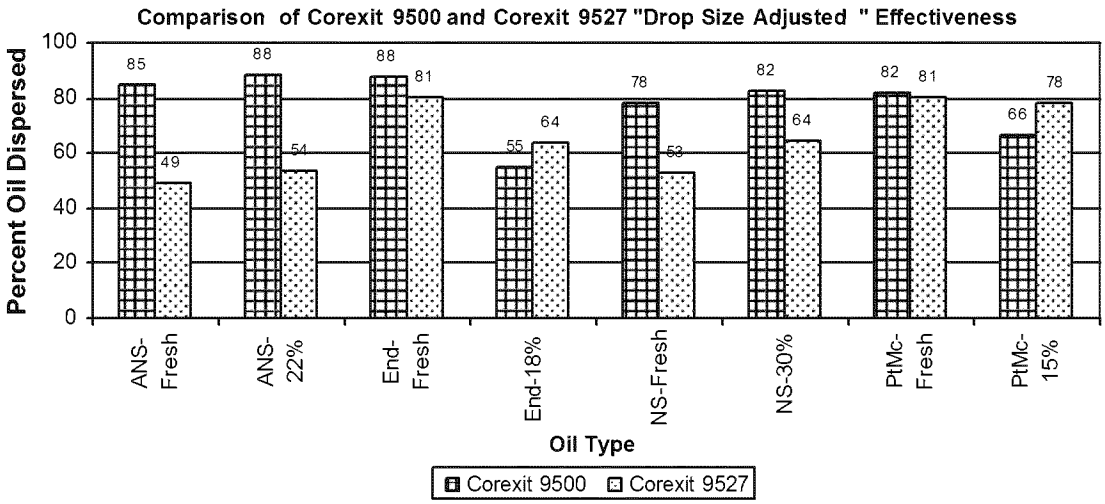


Fig. 6. Comparison of Corexit 9500 and Corexit 9527 "drop size adjusted" effectiveness.

oil drops over time and to estimate a conservative DE value. It should be noted that this adjusted DE may be an underestimate of effectiveness because the oil present in the larger drops held in the water during wave activity may have re-surfaced shortly after the waves were stopped and prior to oil collection and were thus already accounted for in the raw DE estimates. The final "drop size" adjusted DE estimates for the tests are provided in Fig. 6 where the results for the two different dispersants are compared. The adjusted DE results vary from about 50 to 90%. Corexit 9500 appears to have worked better than Corexit 9527 on the ANS (35% higher DE) and Northstar (about 20% higher DE) crude oils (both fresh and weathered) but produced about the same DE on the Endicott and Pt. McIntyre oils (DE values within 10%).

The primary physical oil property that affects dispersant performance is oil viscosity. The drop size adjusted DE values in the two test programs were plotted against initial oil viscosity to determine if there was any correlation between viscosity and DE. There was no trend identified in either test program for the range of viscosities tested. The lack of correlation may be due to the combination of high mixing energy employed (full-scale breaking waves) in the testing and the relatively narrow oil viscosity range tested (5–700 cP).

4.3.2. Oil concentration data: comparison of measurement methods

As previously discussed, four methods were used to document the in-water oil concentration in the 2006 test program; the Turner A10U and Wet Labs fluorometers, the LISST 100 and the Turner TD500. The measurements of in-water oil concentration in the Ohmsett dispersant effectiveness test protocol are made only to provide verification of the presence of dispersed oil in the water column and not to quantify the volume present and, as such, these measurements are of secondary importance. The different measurement methods were deployed in 2006 to permit a qualitative assessment of the various methods for future use in dispersant

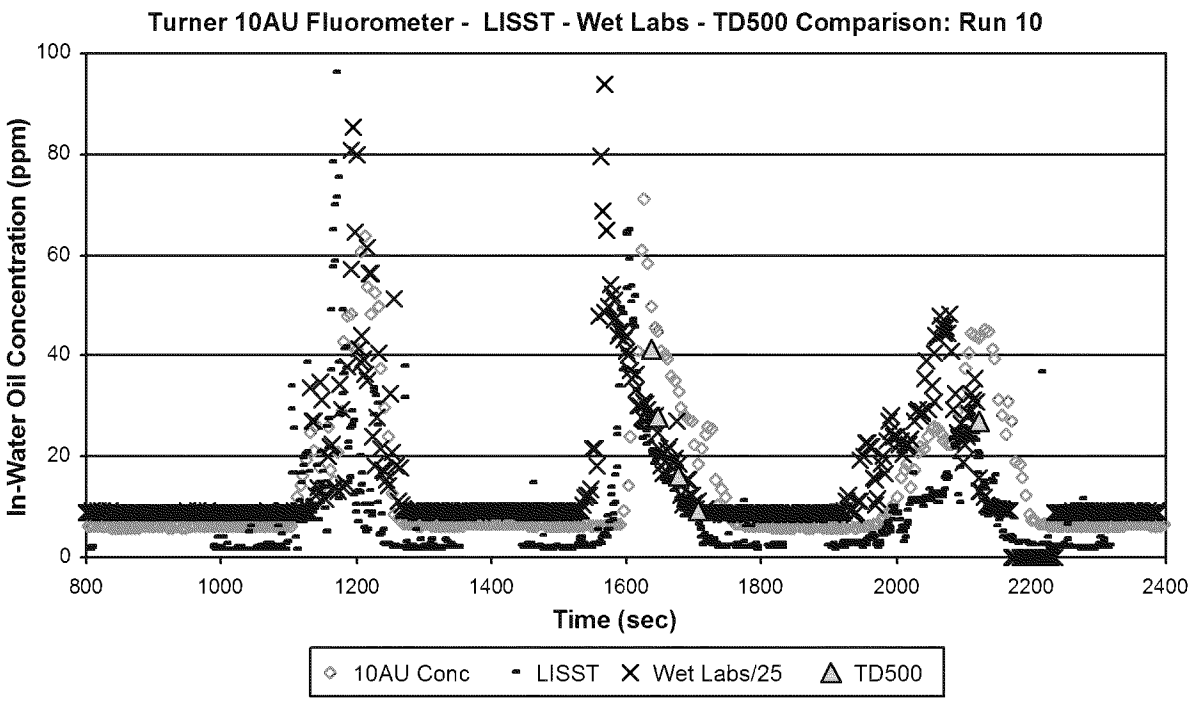


Fig. 7. Comparison of four methods for in-water oil concentration measurement.

testing programs at Ohmsett. Fig. 7 shows a comparison of the four methods used to measure the in-water oil concentration for experiment #10 in 2006. As can be seen in Fig. 7 there was reasonable agreement between the results from the four methods. The TD500 results can be considered the most accurate of these results since a more rigorous oil extraction and calibration procedure was used in determining the oil concentrations by this method.

The Turner 10AU, TD500, TD3100 and Wet Labs fluorometers all require calibration to the specific oil being measured before they can provide estimates of actual oil in-water oil concentrations. Without such calibrations, their outputs provide only relative oil concentration levels within a test. The difficulty of accurately measuring in-water concentrations of dispersed oil using various techniques has been reported elsewhere (Lambert et al., 2001).

The LISST 100 provided a reasonable estimate (similar to the TD500 results) of in-water oil concentration without the need for time-consuming instrument calibration, water sampling, solvent extraction and analysis. The LISST also provides oil drop size distribution information and is therefore a more versatile instrument. Based on the assessments of the various oil concentration measurement techniques used in the 2006 program the LISST 100 was selected for use in subsequent dispersant testing at Ohmsett (including the 2007 test program).

## 5. Discussion

Caution must be used when comparing the results from different DE testing programs because the specific crude oil and dispersant combination used can result in very different DE results. Very seldom is the exact same crude oil used in two independent test programs as even crude oils from a given source (production field or pipeline) constantly change with time. It is known that the properties of ANS crude oil as shipped from Valdez have changed over the past twenty years with a steady decline in both density and viscosity and a decline and then increase in pour point (SL Ross, 2004b). Nevertheless, other researchers have completed dispersant effectiveness tests using fresh and weathered ANS crude oil (of various vintage) and Corexit 9527 and 9500 dispersants under cold conditions. The work that most closely matches that completed in the Ohmsett test basin is the study by (Mackay, 1995) in the ESSO Resources outdoor test basin in cold-water (4 °C) using Alaska North Slope Crude oil and Corexit 9527. The tests completed in this outdoor basin resulted in measured DE values between 80 and 97% for weathered (10–20% evaporated) ANS crude oil that was subjected to breaking waves immediately after the application of dispersant. These results compare very favorably to the "raw" DE estimates recorded in the current study.

The results from other studies that used small bench scale testing do not always correlate to the large scale test results. Mackay (1995) also completed bench scale tests using the Exxon Dispersant Effectiveness Test (EXDET). DE results in the 80%–95% range were recorded using this test on fresh and weathered ANS crude oil at 4 °C. These results are similar to the outcomes recorded in the Ohmsett test series. Moles et al. (2002) used Environment Canada's swirling flask test (SFT) (Fingas et al., 2000) to test the effectiveness of these dispersants on fresh and 20% evaporated ANS over a range of water salinities and temperatures. The SFT results for the both the fresh and weathered oil were below the detection limit of the test (<10%) at the lowest temperature (3 °C) and highest salinity (32 ppt) tested; the conditions that most closely matched those present during the Ohmsett test programs. This is in sharp contrast to even the 50%–90% drop size adjusted DE measured in the Ohmsett test program. The likely explanation for the difference in results is in the degree of mixing energy present in the two test environments. Moles provided the following caution when reporting his results "because our laboratory tests were conducted at low mixing energy, considerable caution should be used in extrapolating these laboratory studies to field conditions". Similar bench scale testing by Fingas et al. (2006) used a slightly modified SFT procedure where only the final oil extraction and detection procedure were modified. Tests were completed on fresh ANS crude oil at 5 °C in 20–30 ppt salinity water and the measured DE ranged from 55 to 65%. These results were considerably higher than those reported by Moles but still not quite as high as the results from the large-scale Ohmsett tests. (Fingas et al., 1991) also reported a SFT DE of only 7% on Prudhoe Bay crude oil, presumably at room temperature, using the SFT procedure. The likely reason for the considerably lower test result compared to his 2006 work is due to the different oil properties of the Alaskan oil in the 15 years between tests.

A comparison of results from various bench-scale DE test methods on heavy fuel oils by Clark et al. (2005) has shown that the swirling flask test (SFT) can generate significantly lower DE estimates than other common bench scale test methods under the same test conditions with the same oils and dispersants. The difference in results is generally attributed to a lower mixing energy in the SFT. Venosa et al. (2005) measured energy dissipation rates in the SFT, EPA's new baffled flask test (BFT), and in the meso-scale wave tank operated by the Canadian Department of Fisheries and Oceans. The energy dissipation rates measured by Venosa et al. in the SFT test were similar in magnitude to those recorded during typical non-breaking wave conditions in the wave tank and the energy dissipation from the BFT were similar in magnitude to those recorded during breaking wave conditions in the tank. While Venosa suggests that this indicates that the BFT test mimics turbulent conditions similar to breaking waves, the work by Mukherjee and Wrenn (2007) indicates that the measurement of energy dissipation alone may not be adequate to describe the differences in dispersant effectiveness and the characteristics of the dispersions that have been observed in experimental systems. These results emphasize the need to be very careful when extrapolating bench-scale DE test results to large-scale or field behavior and supports the use of large scale testing such as that completed in this study to bridge the gap between bench-scale and field-scale testing. This is further supported by Daling and Lichtenthaler (1986) who found poor correlation between the results from three different laboratory DE tests to the results from field tests using the same oils and dispersants.

## 6. Conclusions

The two dispersants tested, Corexit 9527 and Corexit 9500, were both effective (85%–99% raw DE and 50%–90% drop size corrected DE) in dispersing the fresh and weathered Alaskan oils in the large-scale tests completed at the Ohmsett test facility in winter conditions. There was no apparent difference in DE on fresh or weathered oil within the relatively narrow range of viscosities tested (5–700 cP). The results demonstrate that chemical dispersants may be effective in dispersing oils in near freezing water and energetic breaking wave conditions in the offshore environment.

## Acknowledgements

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dispersants. However, no official endorsement from any of these organizations should be implied.

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**To:** Principe, Vanessa[Principe.Vanessa@epa.gov]
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http://www.oilspillprevention.org/~/media/oil-spill-prevention/spillprevention/r-and-d/dispersants/4-toxicity-and-dispersants.pdf

# TOXICITY AND DISPERSANTS

## Things You Should Know

Dispersants included in EPA's list of approved products have low toxicity (EPA Office of Research and Development (ORD), 2010).

Many household products are more toxic than approved dispersants.

Most substances are toxic at some level.

Oil is more toxic than dispersants.

Dispersed oil and dispersants rapidly dilute in the water to concentrations below most acute toxicity thresholds.

Because of enhanced dilution and biodegradation, dispersed oil is less likely to persist and cause chronic effects than untreated oil.

Laboratory tests are used to determine the relative toxicity of different dispersants and to help predict potential effects in the environment.

## Overview

Dispersants are products used in oil spill response to enhance natural microbial degradation, a naturally occurring process where microorganisms remove oil from the environment. All environments contain naturally occurring microbes that feed on and break down crude oil. Dispersants aid the microbial degradation by forming tiny oil droplets, typically less than the size of a period on this page (<100 microns), making them more available for microbial degradation. Wind, current, wave action, or other forms of turbulence help both this process and the rapid dilution of the dispersed oil. The increased surface area of these tiny oil droplets in relation to their volume makes the oil much easier for the petroleum-degrading microorganisms to consume.

Dispersants can be used under a wide variety of conditions since they are generally not subject to the same operational and sea state limitations as the other two main response tools — mechanical recovery and burning in place (also known as in-situ burning). While mechanical recovery may be the best option for small, near-shore spills, which are by far the majority, it has only recovered a small fraction of large offshore spills in the past and requires calm sea state conditions that are not needed for dispersant application. When used appropriately, dispersants have low environmental and human health risk and contain ingredients that are used safely in a variety of consumer products, such as skin creams, cosmetics, and mouthwash (Fingas et al., 1991; 1995).

This fact sheet provides an overview of aquatic toxicity testing and the potential effects that may occur when dispersants are used to respond to oil spilled on water. Toxicity is defined as the "inherent potential or capacity of a material to cause adverse effects in a living organism" and Aquatic Toxicity is the effect of chemicals, materials, and activities on aquatic organisms. The range of these effects is considered from the subcellular level, to whole organisms and even to individual communities and whole ecosystems (Rand, 1995).

## Fact Sheet Series


- Introduction to Dispersants
- Dispersants — Human Health and Safety
- Fate of Oil and Weathering
- Toxicity and Dispersants
- Dispersant Use Approvals in the United States
- Assessing Dispersant Use Trade-offs
- Aerial and Vessel Dispersant Operations
- Subsea and Point Source Dispersant Operations
- Dispersants Use and Regulation Timeline
- Dispersant Use in the Arctic Environment

# Introduction

Large volumes of dispersants were used during the response to the Macondo Well release in the Gulf of Mexico in 2010. Approximately 1.84 million gallons (7 million liters) of dispersants were used at the surface and subsurface (Lehr et al., 2010). Prior to this, the largest use of dispersant was during the 1979 IXTOC-1 spill in the Bay of Campeche, Mexico where 1 to 2.5 million gallons (~4 to 10 million liters) of dispersants were applied over a five-month period (EPA online, 2011). With the quantities of dispersant applied during the Macondo response and for responses in the past, the government and public continue to question the impact that oil and dispersed oil may have on the environment. Scientists have studied the effects of oil, dispersants and dispersed oil on organisms in the marine environment for more than 30 years.

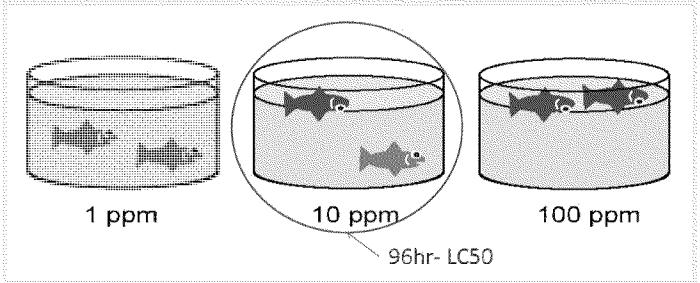
Research efforts often focus on measuring the aquatic toxicity of dispersants on standard test organisms, such as fish and shrimp (EPA ORD, 2010). Adverse effects can include changes to behavior, physiology (such as slowed movements), reproduction (such as reduced fertility), or possibly death when in the presence of certain concentrations of the test materials. Observed effects are a function of both the duration of exposure to the chemical and the concentration of the chemical during the length of the test. In the actual aquatic environment, the length of exposure varies with tides and currents and the mobility of the potentially affected organism, while the concentration of a chemical is heavily influenced by the following:

- Physical, chemical, and biological properties of the ecosystem, such as salinity, temperature, water depth, waves, and currents, which will influence vertical and horizontal mixing in the water column.
- Sources and rate of input of the chemical into the environment.
- Physical (e.g., boiling point, viscosity) and chemical (e.g., elemental composition) properties of the chemical.

Observed effects can be produced by short-term (acute) or long-term (chronic) exposure. In the case of oil spills, the potential for negative effects from short-term exposure would be expected to occur early in the spill. This is because some of the smaller, more volatile molecules in the oil are quickly lost by evaporation but also can readily dissolve into the underlying water creating short term aquatic toxicity before being diluted and degraded naturally. Alternatively, long-term exposures generally involve exposure to decreased amounts of the larger compounds found in oil that are less toxic.

The toxicity of a substance is also relative, and often, species dependent. Testing can be used to produce some basic relative categorizations about the toxicity of substances. For example, the lethal concentration to 50% of the test organisms ($LC_{50}$) is often used as a measure of aquatic toxicity (Figure 1).

FIGURE 1. Example of an $LC_{50}$ test showing the concentration of a chemical that will kill 50 percent of the animals tested.
Source: A. Bejarano, 2012.




# Measuring Toxicity

Essentially, all substances have some ability to lead to toxic or adverse effects which are directly related to concentration and length of exposure. The "adverse effects" are responses exhibited outside the normal range for healthy organisms. In an effort to understand the adverse effects of oil, dispersed oil, and the dispersant itself, the EPA and other agencies evaluate the aquatic toxicity of an exposure over a specified period of time.

NOTE:

The reader is cautioned that laboratory aquatic toxicity tests are NOT representative of the likely exposures experienced by organisms in an environment that is affected by spilled oil. Natural weathering processes like spreading, evaporation, and dilution occur which serve to reduce the potential exposure duration and concentration to well below those used in toxicity tests; refer to Fact Sheet 3 — Fate of Oil and Weathering for more information on how oil behaves and changes over time.

A laboratory test only allows a relative comparison between the aquatic toxicity of various chemicals and is not an evaluation of potential impacts to organisms in the environment.

Toxicity tests are used to help predict the potential adverse effects of chemicals on aquatic organisms or humans. When measuring toxicity under laboratory conditions, the goal is to estimate what concentrations of a chemical cause a specific



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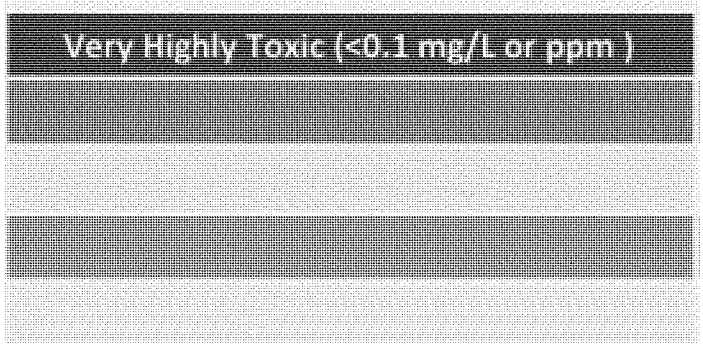
effect over a specific period of time. These may be either short-term or long-term tests. All quantitative aquatic toxicity assessments are based on the dose-response concept (typically measured in parts per million [ppm] or mg/L; and parts per billion [ppb] or µg/L). As the dose (exposure) to a chemical increases, so does the potential for a negative response. When comparing chemicals side-by-side, the *more* chemical it takes to cause an acute effect, the *less* toxic the chemical is.

The US EPA (EPA online, 2012) has established the following scale (Figure 2) for interpreting laboratory-generated aquatic toxicity information using $LC_{50}$ values (mg/L = ppm).

FIGURE 2 US EPA's $LC_{50}$ aquatic toxicity scale for laboratory-generated aquatic toxicity data. Source: EPA online, 2012.




The aquatic toxicity results for two key test species (mysid shrimp and silverside, a small fish also known as *Menidia*) as determined by EPA for the Macondo response are shown for the Macondo Well crude oil, the dispersant Corexit® EC9500A, and the oil-dispersant mix (Table 1).

Furthermore, the US EPA evaluated the eight commercially available dispersants and found that the dispersants tested had different levels of toxicity, but the major product used, Corexit® EC9500A, was among the least toxic. Ultimately, the crude oil by itself was found to be more toxic to the test species than the dispersants alone; the dispersants alone were less toxic than the dispersant-oil mixture; and the oil alone displayed toxicity results similar to the dispersant-oil mixtures (EPA ORD, 2010).

## Influences on Toxicity of Oil-Dispersant Mixtures

Although tests can be used to produce a numerical measure of a substance's aquatic toxicity and provide important information about the effects of oil and dispersants, many of these tests do not accurately reproduce the different types of exposures organisms may experience during an actual oil spill. For example, when dispersants act to break up the oil into droplets, moving the now dispersed oil from the water surface downward into the water column, oil exposure will typically decrease for surface-dwelling and intertidal organisms, but increase for water column and possibly, bottom-dwelling organisms, for a period of time. In general, concentrations in the water column are expected to decrease fairly rapidly, i.e., within a matter of hours. This is different from test protocols which typically use a constant concentration over a fixed amount of time (typically 48 to 96 hours).

Any detectable or measurable response of an organism in a laboratory toxicity test should not be interpreted as resulting

TABLE 1 EPA's aquatic toxicity testing summary results for the spilled oil, dispersant, and dispersed oil from the Deepwater Horizon Response (EPA ORD, 2010).

| | Louisiana Sweet Crude (LSC) Oil | | Dispersant (Corexit 9500) | | Dispersed Oil (LSC + Corexit 9500) | |
|---|---|---|---|---|---|---|
| Species Tested | Mysid Shrimp | *Menidia beryllina* (Fish) | Mysid Shrimp | *Menidia beryllina* (Fish) | Mysid Shrimp | *Menidia beryllina* (Fish) |
| Very Highly Toxic | | | | | | |
| Highly Toxic | | | | | | |
| Moderately Toxic | 2.7 ppm | 3.5 ppm | | | 5.4 ppm | 7.6 ppm |
| Slightly Toxic | | | 42.0 ppm | | | |
| Practically Non-toxic | | | | 130.0 ppm | | |



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in a similar effect in the environment (Rand, 1995). During an actual incident, there are many factors that can change the effects that oil-dispersant mixtures may have. These factors can include:

- Differences in length of exposure. Length of exposure can vary greatly over time, as tides change or currents shift. Exposure may increase, decrease, or even stop. Exposure also varies between intertidal, surface and water column organisms.
- Volume of dispersants or oil-dispersant mixtures. Higher volumes may result in increased exposure to dispersed oil.
- Weather. Depending on sea state, oil-dispersant mixtures may spread out faster, deeper, further, and become more diluted quite quickly.
- Weathering. Changes the oil undergoes as a result of natural processes.

Laboratory tests give very conservative estimates of potential exposure effects to resources in the water column. The use of a spiked/declining dose "flow-through" toxicity test provides a more realistic means of evaluating the likely exposure of resources in the environment but it is not the normal procedure for most studies (ASTM, 2007a & 2007b; Rand, 1995).

## Toxicity of Dispersants and Oil-Dispersant Mixtures

There are many complicating factors in the measurement and prediction of toxicity related to specific spill conditions. Many studies have evaluated the aquatic toxicity of crude oils, dispersants, and oil-dispersant mixtures. These studies indicate that dispersants are less toxic than oil itself (EPA ORD, 2010; NRC, 2005).

However, dispersants do increase the local concentration of oil in the water column for a period of time. This does not alter the toxicity of the oil, however, the potential exposure is increased for resources in the water column, at least until mixing and natural dilution occur and reduce the concentration. Potential toxicity of dispersants to humans is just as difficult to determine, especially when it is known that each dispersant formulation is composed of a different group of chemicals. However, public exposure along shorelines is unlikely, since dispersants are generally only applied more than three miles from shore by boats and planes using specialized equipment. For more information on the potential toxicity to humans (responders and the public) refer to Fact Sheet #2 — Dispersants — Human Health and Safety.

In summary, there is public and regulatory concern about the toxicity of the dispersant in conjunction with the oil itself in the environment. This fact sheet indicates that concern is often unwarranted as research has shown that it is the oil that is the toxic component in the exposure. Although dispersants may locally increase the oil concentration in the water column for a period of time, the large dilution potential where dispersants would be applied serves to lower the overall oil exposure duration experienced by water column organisms.

Lastly, using a Net Environmental Benefit Analysis (NEBA) approach, it is important to compare such impacts to water column organisms with those impacts to surface animals and shoreline habitats that would occur if the oil were not dispersed but remained on the water's surface. For more information on this approach, refer to Fact Sheet #6 — Assessing Dispersant Use Trade-offs.

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**To:** Principe, Vanessa[Principe.Vanessa@epa.gov]
**From:** Wilson, Gregory
**Sent:** Wed 2/4/2015 6:15:56 PM
**Subject:** FW: Draft Minutes - ICCOPR FY2015 First Quarterly Meeting
Draft Minutes ICCOPR FY15-1st Quarter Meeting For Review.pdf
9 - USACE Oil Spill Research update.pdf

-----Original Message-----
From: William.T.Vocke@uscg.mil [mailto:William.T.Vocke@uscg.mil]
Sent: Wednesday, February 04, 2015 1:13 PM
To: Vocke, William CIV
Subject: Draft Minutes - ICCOPR FY2015 First Quarterly Meeting

ICCOPR Members,

Attached are the draft minutes for ICCOPR's FY2015 First Quarterly Meeting, which was conducted at Coast Guard Headquarters on January 22-23, 2015. Also attached is the USACE R&D Update, which was provided for the record after the meeting. All other enclosures were provided in earlier emails and are not enclosed due to their size.

Please review the minutes and provide any comments to me by COB February 20, 2015.

I want to thank all 34 participants for their contributions to an interesting and enlightening meeting. For those of you who attended in person, I also thank you for your patience in getting through security and navigating the maze inside the building. I welcome any feedback on using the Coast Guard Headquarters as a meeting site and what we could do to make it better.

Bill

William T. Vocke
ICCOPR Executive Director
U.S. Coast Guard - Stop 7516
2703 Martin Luther King Jr. Ave. SE
Washington, DC 20593-7516
(202) 372-2019

USACE Oil Spill Research for 22-23 January 2015 ICCOPR Meeting

The US Army Corps of Engineers' Engineering Research and Development Center's (ERDC's) Cold Regions Research and Engineering Laboratory (CRREL) is engaged in evaluating the ability to detect oil on and under ice. The work includes remote sensing and instruments to address the question of how far into the ice aerial systems can "see" and also what happens to the oil (and detection) as a function of time. Experiments started after Thanksgiving where examination include detection of oil in growing ice and is addressing oil detection during the decay phase. Radar, acoustic, fluorometer, and microwave systems are being evaluated. The performance of pipes, pumps, and gaskets under the stress of low temperatures is also being examined.

A group from Alaska Clean Seas will be coming to CRREL the week of 26 January for training in the use of skimmers. Additional information can be found at:

http://www.arcticresponsetechnology.org/wp-content/uploads/2013/10/jip-ig-remotesensing.pdf

http://www.arcticresponsetechnology.org/project-updates/oil-spill-detection-and-mapping-in-low-visibility-and-ice/first-of-its-kind-remote-sensing-experiments-commence

**To:** Vocke, William CIV[William.T.Vocke@uscg.mil]
**From:** William.T.Vocke@uscg.mil
**Sent:** Wed 2/4/2015 6:12:40 PM
**Subject:** Draft Minutes - ICCOPR FY2015 First Quarterly Meeting
Draft Minutes ICCOPR FY15-1st Quarter Meeting For Review.pdf
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# Regulations relating to the composition and use of dispersants and beach-cleaning agents to combat oil pollution

*Laid down by the Ministry of the Environment on the 10 of October 2001 pursuant to section 4, first paragraph, litra a) and c) of Act of 11 June 1976 No. 79 relating to the control of products and consumer services, cf. Royal Decree of 7 September 1990 No. 730 and section 40 of the Act of 13 March 1981 No. 6 relating to protection against pollution and relating to waste, cf. Royal Decree of 8 July 1983.*[1]

**§ 1 Purpose of the regulations**

The purpose of these regulations is to reduce the environmental impact of acute oil pollution.

**§ 2 Range of application**

The regulations apply to the composition and use of chemical dispersants and beach-cleaning agents to combat acute oil pollution.

**§ 3 Definitions**

A dispersant is a liquid, chemical solution which when applied to a slick of oil on the water surface, accelerates the break-up of an oil slick into small droplets of oil which are diluted and broken down in the water column.

A beach-cleaning agent is a liquid, chemical solution which causes the oil to separate from the underlying surface and possibly disperse in the water column when it is hosed off the beach.

**§ 4 Requirements applicable to dispersants and beach-cleaning agents**

A product that is to be used as a dispersant or a beach-cleaning agent shall be tested for acute toxicity and satisfy the requirements, cf. Annex 1, clause/article/item 1 to these regulations. The effectivity of the product shall be tested, and the most effective product shall be used, cf. Annex 1, clause/article/item 2 to these regulations.

The user of a dispersant or a beach-cleaning agent is responsible for ensuring that the products used satisfy the requirements pursuant to the first paragraph of this section at all times.

**§ 5 Use of dispersants and beach-cleaning agents**

The use of dispersants and beach-cleaning agents in activities to which section 6 does not apply, requires a special permit from the Norwegian Pollution Control Authority. Users are required to hold such a permit before the dispersant or beach-cleaning agent is applied.

If an unacceptable threat of human life or health should arise in connection with an oil spill, dispersants may be used without a special permit. Such use is to be reported to the Norwegian Pollution Control authority as soon as possible after the incident. The report shall include a description of the incident, and volume and type of dispersant used.

The use of dispersants or beach-cleaning agents shall be chosen when this method, in comparison with other methods, results in minimum overall damage to the environment yet does not involve unreasonable costs.

The user is responsible for ensuring that an unsuccessful dispersion operation is

[1] Notificated the EEA Agreement pursuant to Council Directive 98/34 of the European Parliament



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stopped immediately.

**§ 6 Use of dispersants and beach-cleaning agents in accordance with a contingency plan**

Anyone engaged in activities for which a contingency system is required, cf. section 40 and section 43 of the Pollution Control Act, may use dispersants and beach-cleaning agents in accordance with (pursuant to) their contingency plan.

**§ 7 Planning and documentation**

An assessment of the potential adverse environmental impact and the effectiveness of dispersants and beach-cleaning agents shall be made before use.

The user must ensure that the necessary documentation regarding the dispersants effectiveness and use is available, cf. Annex 2 to these regulations.

The user is responsible for ensuring that written documentation of this assessment is available.

**§ 8 Requirements for dispersant application equipment**

All application equipment planned to be used during an oil spill clean-up operation shall be tested in practical trials to ensure that the equipment and procedures for application function as intended.

**§ 9 Exceptions and amendments**

The Norwegian Pollution Control Authority or the instance thereby authorized by the Ministry of the Environment may, in special instances make exceptions from the provisions of these regulations.

The Norwegian Pollution Control Authority may amend the annexes to these regulations.

**§ 10 Control**

The Norwegian Pollution Control Authority or the instance thereby authorized by the Ministry of the Environment will be responsible for ensuring compliance with these regulations.

**§ 11 Appeals**

Individual decisions made by the Norwegian Pollution Control Authority pursuant to these regulations may be appealed to the Ministry of the Environment.

**§ 12 Penal measures**

Any contravention of these regulations or decisions made pursuant thereto may be penalized in accordance with section 78 of the Pollution Control Act unless the offence is subject to a more severe penalty.

**§ 13 Entry into force and transitional provisions**

These regulations enter into force on January the 1st 2002. As of the same date the Regulations concerning the composition and use of dispersants to combat oil pollution, laid down by the Ministry of the Environment on 2 February 1980, are repealed.

Dispersants and beach-cleaning agents approved pursuant to these previous regulations may be used until January the 1st 2003.



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# ANNEX

## ANNEX 1: Acute toxicity and effectiveness – tests and requirements

All tests are to be performed in an accredited laboratory and with reference to good laboratory practice (GLP).

*1. ACUTE TOXICITY*

Both dispersants and beach-cleaning agents shall be tested on:

Planktonic algae:
The test procedure is described in the OSPAR Guidelines for Completing the Harmonized Offshore Chemical Notification Format (HOCNF) and in the procedure ISO/DIS 10253 (*Skeletonema costatum*).

Requirements:
The use of dispersants is prohibited if $EC_{50}$ < 10 mg/l.
The use of beach-cleaning agents is prohibited if $EC_{50}$ < 100 mg/l.

*2. EFFECTIVENESS*

**A. Activities that involve the production or processing of oil**

Tests:
An IFP (Institute Francais du Petrole) test shall be used to compare relevant dispersants as described in *Bocard et.al. (1984): Chemical oil dispersion in trials at sea and in laboratory tests: the key role of dilution processes. In: Oil Spill Chemical Dispersants: Research, Experience and Recommendations, STP 840, Tom E. Allen, Ed., American Society for Testing and Materials, Philadelphia, pp. 125 – 142, 1984.*

For tests of the dispersibility of oil that has undergone varying degrees of weathering, the IFP test shall be used in combination with an MNS (Mackay, Nadeau and Steelmann) test as described in *Mackay, D., Szeto, F. 1981: Effectiveness of oil dispersants – development of a laboratory method and results for selected commercial products. Institute of Environmental Studies, University of Toronto, Publ. No. EE – 165.*

Test procedures are described in Annex 2.

**B. Activities that do not involve the production or processing of oil**

Test:
A WSL (Warren Spring Laboratory) test shall be used as described in *Martinelli, F.N., 1984: The status of the Warren Spring Laboratory's rolling flask test. In: Oil Spill Chemical Dispersants: Research, Experience and Recommendations. STP 840. Tom E. Allen, Ed. American Society for Testing and Materials, Philadelphia, pp. 55 – 68, 1984.*

Test procedures are described in Annex 2.

**Requirements regarding 2A and 2B:**

Test documentation for both types of test shall clearly indicate whether the dispersant or beach-cleaning agent has been tested for normal or low salinity conditions. No limit for minimum effectiveness has been set, as the effectiveness of a dispersant/ beach-cleaning agent will vary in relation to oil type.



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# ANNEX 2: Procedures for testing the effectiveness of dispersants/beach-cleaning agents

## A. Activities that involve the production or processing of oil

In the case of activities that involve the production, processing or storage of specified types of oil and where dispersants/ beach-cleaning agents are intended to be used as part of the contingency system, the effectiveness test shall be conducted using these oils. If so many types of oil are produced or processed by the same enterprise that effectiveness testing of all the oils will incur unreasonably high costs, testing shall be conducted on a selection of the types of oil most likely to be treated by dispersion. In order to optimise the enterprise's emergency response, a screening should first be made of suitable dispersants/ beach-cleaning agents on the basis of type of oil produced or processed by the enterprise, local conditions with regard to temperature and salinity, and form of technical application.

### Test programme for product optimisation

Product optimisation includes:

1. Screening of products approved according to the procedures described in B. (*Activities that do not involve the production or processing of oil*). The selected products at 200°C/50% emulsion of the relevant oil is tested with the IFP test. 3 parallels for each product, with dosage ratio1:25.
2. Testing of the three best products in varying dosage ratios at 200°C/50%: (e.g.1:25, 1:50 and 1:100). 3 parallels for each product and dosage ratio.
3. Testing of the three best products at an alternative temperature and salinity: 200°C/50% emulsion, dosage 1:25. 3 parallels for each product.

### Test programme to ascertain dispersibility of oil, which has undergone varying degrees of weathering

Two different test methods (IFP and MNS) shall be used to test dispersibility on several different samples of the oil, which represent varying degrees of weathering.

## B. Activities that do not involve the production or processing of oil

Activities for which a contingency system is required but for which it is not possible to specify any particular types of oil, shall be able to plan a contingency system using dispersants/ beach-cleaning agents if a "standard" test procedure has been conducted.

In this standard test procedure, the WSL test shall be used.
The test procedure shall be conducted under the following conditions:

| Test oil | Conditions |
|---|---|
| 1 Sture Blend 200°C/50% | 10°C, 3.5% salinity |
| 2 Medium Fuel Oil (2000 cP at 10°C) | 10°C, 3.5% salinity |
| 3 Sture Blend 200°C/50% | 10°C, 0.5% salinity |

The first two tests shall be run for all the products to be used. The third test need only be conducted if there are plans to use the product at low salinity. A dosage ratio (DOR) of 1:25 shall be used in all the tests.



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## COMMENTS

**Re § 2**

The regulations regulate the composition and use of chemical dispersants and beach-cleaning agents and apply to operations to combat acute oil pollution on the water surface or on the shoreline, in fresh water and sea water, from ships, from land-based activities and from activities on the continental shelf, regardless of the size of the oil spill.

The regulations are directed towards persons who use or who plan to use dispersants or beach-cleaning agents to combat acute oil pollution.

**Re § 3**

Dispersants may be used to disperse oil in the water column so that it is more readily available for degradation by micro-organisms. Chemically dispersed oil does not sink but is dispersed in the water column. Dispersion of oil in water is therefore a process of dilution, which prevents the oil from adhering to macro-organisms and substrate at and on the surface of the water.

There are two main types of beach-cleaning agents. One of these types is like a dispersant in that it causes the oil to unfasten from surfaces to which it has adhered and then disperses the oil in the water when it is hosed off the beach. The other type causes the oil to unfasten from surfaces to which it has adhered and may then be recovered mechanically from the surface of the water when hosed off the beach. Assessment of which of the two types of agent should be used in each individual case must be made on the basis of the vulnerability of the environment, the possibilities of further treatment of the oil and water exchange in the areas where the dispersant is applied.

**Re § 4**

The use of a dispersant/ beach-cleaning agent shall involve as little impact on the environment and on the people working with it as possible. As soon as internationally accepted methods of testing for the bioaccumulation potential of surfactants have been documented, such testing will be required.

Toxicity testing of dispersants using planktonic algae is required, cf. Annex 1. The environmental authorities have selected the test organism and test that are described in the OSPAR test system. There is international agreement on the use of this system for toxicity testing of chemicals used offshore. The environmental authorities have set a limit for the toxicity test to give a maximum level for how environmentally toxic a dispersant or beach-cleaning agent may be before use is no longer permitted.

The effectiveness of dispersants and beach-cleaning agents will vary to a great extent depending on the kind of oil they are used to treat. Even though testing products for effectiveness is required, it would serve no purpose to set specific minimum limits for effectiveness when the type of oil the product will be used on is not specified. It is the users responsibility to use the most effective product for the spesific oil types in question.

Effectiveness testing of dispersants is conducted either using types of oil that are typical for Norwegian conditions (bunker oils and a typical North Sea oil) or the types of oil relevant to enterprises required to have a contingency system. If a potential user buys a dispersant without knowing exactly which oil it is going to be used on, the dispersant must be tested for effectiveness on representative "standard" test-oils. Enterprises in the process of building up a contingency system for oil pollution within the enterprise, where the type or types of oil are known, must conduct tests using these specific oils. Enterprises that process many types of oil are required to test the types of oil that the dispersant is intended to be used on. For enterprises that deal with so many types of oil that the cost of testing all of



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them would be unreasonably high, the enterprise itself must make a reasoned selection of types of oil for testing. For the offshore industry, this selection will be based on regulations concerning internal control, and provisions concerning contingency planning for acute pollution in the regulations relating to health, environment an safety in the petroleum activities.

The physical properties of the dispersant will affect its performance. In cold weather the performance of water-soluble dispersants in particular may change. The use of helicopter buckets and other spraying equipment also require dispersants with a certain minimum viscosity. Whether the performance qualities of the dispersant change after a certain time in storage should also be checked. As a rough guideline, the following figures may be used to describe a "user-friendly" dispersant:

| | |
|---|---|
| Viscosity: | 50 – 250 cP at 0°C |
| Flash-point: | > 60°C (according to ASTM D Method 93 / IP 34) |
| Storage test: | No precipitation of components after a 7-day storage test at 15°C using the IP method, and cloud point at < -15°C according to ASTM D Method 2500 / IP 219 |

It is emphasized that it is the user's responsibility to ensure that the correct dispersant is used and that it is used in accordance with these regulations. The environmental authorities will ask additional questions to verify this in connection with the approval of contingency plans, audits or exercises and in connection with the use of dispersants during clean-up operations. The user must therefore ensure that all the necessary documentation about the dispersant that is being used is available, cf. section 7.

**Re § 5**

If a pollution situation arises in which the use of dispersants or beach-cleaning agents could reduce the environmental impact and for which it has not been reasonably possible to plan, application may be made for a special permit to use dispersants or beach-cleaning agents.

Applications in accordance with the first paragraph of section 5 will be dealt with via the Norwegian Pollution Control Authority's 24-hours-a-day standby.

Acute hydrocarbon pollution can cause situations with unacceptable risk of human life or health, for instance when there is danger of fire or explosion. In such instances dispersant or beach-cleaning agents may be used without a special permit. The use is to be reported to the Norwegian Pollution Control Authority subsequently.

Anyone who takes action against acute oil pollution shall choose the most environmentally beneficial response method or methods that result in an overall least impact on the natural environment. The use of dispersants and beach-cleaning agents shall therefore act as both an independent alternative and a supplement to other methods of emergency response.

The use of dispersants and beach-cleaning agents must be critically assessed. The criteria set out in section 5 of these regulations must therefore be viewed as a basis for assessment regarding the correct use of a dispersant.

Dispersants and beach-cleaning agents shall be used to accelerate the natural degradation of oil at sea and in coastal waters. It is important that the dispersant is not used on loose or porous surfaces where the dispersed oil may be absorbed into the substrate.

A general rule for the application of a dispersant on oil at sea is to apply the dispersant in the ratio 1 volume of dispersant to 10 volumes of oil unless a prior assessment indicates otherwise. However, many modern dispersants are very effective on particular



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types of oil and other ratios by volume may apply.

The dispersant should be applied on the thickest parts of the oil slick, which are often at the leading edge. Weather and wave conditions shall be taken into consideration during application. In the case of wave heights below 0.5 m, it may be an advantage to stir the mixture of oil and dispersant so as to establish good contact between the two. In the case of wave heights above 2-3 m and breaking waves, the wave energy will probably be sufficient to disperse the oil. Using a great deal of mixing energy to apply dispersants would therefore be unnecessary.

The use of dispersants in lakes and rivers with a limited volume of water has previously been prohibited because the volume of available water is often too small for the dispersed oil to be sufficiently diluted. However, the environmental authorities can envisage periods of the year in which the use of dispersants in large lakes or rivers when the discharge volume is high may be justified. In the event of proposals to use dispersants in this way, any potential danger to the environment will be carefully assessed in connection with the Norwegian Pollution Control Authority's review of contingency plans.

Monitoring made from aircraft may be very useful when assessing how effective an application has been and such observations should be used whenever possible. In many cases, it may take time before the dispersant produces a visible effect. This applies in particular if the oil has weathered to a certain extent and has formed emulsions. In these cases the dispersant needs time to penetrate the emulsion and start the process of dispersion.

**Re § 6**

The purpose of these regulations is to permit the planned and documented use of dispersants and beach-cleaning agents, and at the same time to introduce stricter rules to prevent unregulated and unnecessary use. Those engaged in activities for which a contingency system for acute pollution is obligatory, will be able to use dispersants or beach-cleaning agents if the use of these preparations has been planned for as part of an approved contingency plan. All other use of these substances is prohibited unless a special permit for their use has been issued by the Norwegian Pollution Control Authority (cf. section 5).

Under the Pollution Control Act the environmental authorities may impose special requirements with regard to the use of dispersants and beach-cleaning agents on those engaged in activities for which a contingency system is required. The authorities may give direct orders to establish a contingency system based on dispersants if it is thought that this will reduce the damage caused by an oil spill. More specific requirements will be imposed where necessary when the contingency plan is reviewed. The contingency plan shall indicate where dispersants and beach-cleaning agents may be used in relation to vulnerable environmental resources that have been mapped and ranked in terms of priority. Factors that shall be taken into consideration when priorities are being decided are time of year, natural purification and alternative forms of response.

**Re § 7**

An evaluation of the potential environmental damage caused by the use of dispersants or beach-cleaning agents must be carryed out before use. This includes an evaluation of the natural resources in the area which can be affected by the dispersed oil, compared to the potential damage of the oil when dispersants or beach-cleaning agents is not used as a combat measure. The effectivness of specific products on the oil that is to be dispersed must be evaluated cf required test procedures. Enterprises with an approved contingency plan with defined terms of use of dispersants or beach-cleaning agents may use this measure of combat when the terms are fulfilled. If the terms of use is not described



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beforehand, the user must submit such an evaluation to the Norwegian Pollution Control Authority to get a special permit according to the firsth paragraph of section 5.

**Re § 8.**

When the decision has been taken to disperse an oil slick, it is important to begin application of the dispersant as soon as possible so as to achieve the best possible effect. The dispersant shall be applied in a specific ratio to the volume of oil, using thoroughly tested equipment. The amount of dispersant per area of oil slick should be controlled by having trained personnel to apply the dispersant and preferably monitoring the operation from the air.

Many of today's dispersants are applied as concentrates. Modern concentrates may therefore be too viscous to achieve optimal application if older equipment, designed for application of diluted dispersants, is used. It is important that the user makes sure that the equipment is intended for use with the type of application planned.

**Re § 9**

In special cases, after an overall assessment of the situation, the Norwegian Pollution Control Authority may decide to grant exemptions from the provisions of these regulations.

These regulations require testing of acute toxicity and effectiveness. These procedures are the subject of international discussions and agreements and may change as new knowledge is acquired. The authorities have therefore the right to amend the annexes to these regulations in keeping up with the increase in knowledge.

**Re § 10**

Control to ensure compliance with the provisions of these regulations will be carried out in connection with contingency planning, exercises, audits, contingency operations and the authorities' general supervisory and control activities.

The Norwegian Pollution Control Authority, or the instance thereby authorized by the Ministry of the Environment, may at any time require access to documentation describing when and how dispersants or beach-cleaning agents are planned or when they have been used in accordance with these regulations. The Norwegian Pollution Control Authority will seek to inspect these matters during its regular control activities.



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*Helcom – Dispersant workshop, April 26. – 27th. 2005*

# Norwegian regulations to dispersant use

Per S. Daling, (per.s.daling@sintef.no)
SINTEF, Marine Environmental Technology Dept.

- **Attitude**
- **New Regulations**
- **Requirements to dispersants**
- **Documentations needed for contingency planning**
- **Decision making**



# Organization of Norwegian Oil spill Preparedness

**Responsibility divided into:**

1. **Municipal (IUA) (smaller spills)**
2. **State (Governmental – NCA –Coastal Adm.) provide support to the municipalities in larger oil spill situations along the coast**
3. **Private Preparedness:**
   - Operators on Norwegian Continental Shelf (Field contingency + NOFO)
   - Crude Oil terminals / Refineries
   - Companies distribution oil products
   - Major industrial companies



# Use of dispersants in Norway

- **Mechanical recovery has traditionally been the primary oil spill response strategy in Norway**
- **Recent years signals from the Authorities:**
  "Dispersants should be a more operational alternative / supplement in certain oil spill situations" i.e:
  where dispersants are considered to give the overall most environmentally benefit (NEBA-philosophy)
- **New regulations for use of dispersants (2002)**
  - ⇨ Oil industry: preparing contingency plans including pre-approval use of dispersants in specific regions / locations: refineries, oil terminals and off-shore fields
  - ⇨ The Government (NCA) is planning to build up a dispersant contingency along the coast over the coming 3-4 years



# Norwegian regulations for use of dispersants

- Founded on the principle of *"internal control".*
- The enterprise (user) responsible for the oil spill operation have to produce pre-planned documentation that must be followed in an eventual spill response.
- The documentation must be available as part of an approved contingency plan: Based on analyses of relevant spill scenarios (different spill amount, different response options etc).
- These scenario-based contingency plans should demonstrate if the use of dispersants will be the best overall response for the environment in the given spill situation (NEBA-approach)





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## Why change in the attitude to use of dispersants in offshore water in Norway ?

**A result of R&D – programs in Norway → new scientific documentation:**

- Better methodology for characterising oils weathering at sea
- Methodology for predicting "time window" for use of dispersants
- Development of more effective dispersants
- Improved dispersant application technology
- Better operational model tools for use in NEBA and cont. planning
- Series of field trials in Norway with dispersant application



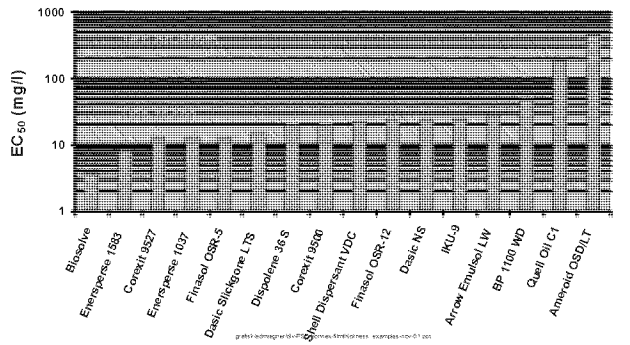
*New Norwegian regulations*

## Requirements to dispersants (§4):

**1. Acute toxicity testing of Oil Spill Dispersants :**

PARCOM: ISO/DP 10253 (*Skeletonema costatum*)

Acceptance criteria: EC50 > 10 mg/l Dispersant (concentrates) at sea
EC50 > 100 mg/l Beach Cleaners/Dispersant shoreline (preliminary)






**Norwegian regulations – requirements to dispersants (§4):**

## For a users processing oils

**(responsible for contingency / response)**

- Dispersant performance (effectiveness) has to be documented by the user (enterprise)
- Part of the user's contingency plan (offshore oil fields / Oil terminals / refineries)

**Dispersant performance documentation :**

- To be tested on "their" specific oils (weathered / emulsions)
- Three steps :
  1. Screening of 5 - 8 dispersants (DOR = 1 / 25) (IFP)
  2. Dosage test (3 best dispersants) (IFP)
  3. Dispersibility vs. increased weathering. Basis for:
     - defining upper viscosity limit for chemical dispersibility
     - basis for predicting the "time window" effective use of dispersant use under different sea conditions



**Norwegian regulations – requirements to dispersants (§4):**

## For governmental preparedness (non-specific oils)

- **Plan a contingency for dispersant use based on a "standard" test procedure:**

| Test oil | Conditions |
|---|---|
| 1. Sture Blend 200°C+ / 50% water emulsion | 10°C, 3.5% salinity |
| 2. Medium Fuel Oil (2000 cP at 10°C) | 10°C, 3.5% salinity |
| 3 Sture Blend 200°C+ / 50% water emulsion | 10°C, 0.5% salinity |

The third test need only be conducted if there are plans to use the product at low salinity. Test: WSL, Dosage ratio (DOR): 1:25 .

No pre-approved list of dispersants are maintained by the authorities

Norwegian regulations – requirements to dispersants (§4):

## Physical – chemical requirements:

- Viscosity: 50 – 250 cP at 0°C
- Flash-point: > 60°C ( to ASTM / IP method)
- Storage test:
  - No precipitation after a 7-day storage test at - 15°C (IP method)
  - Cloud point at < -15°C (ASTM / IP method)
- Composition:
  - Biodegradable compounds
  - no toxic / carcinogenic compounds e.g: no halogenated (PCB) aromatics (< 5%)



## Dispersants in stock - what may happen during long-term storage ?

- **Manufacturers generally grants 5 years under "optimal" conditions**
- **Optimal storage conditions:**
  - stored in original sealed containers (0.2-3 $m^3$ )
  - Temperatures: -20 - + 30°C
- **Storage in tanks on ships:**
  **Possible degradation of the dispersant performance:**
  - Oxidation of surfactants
  - Evaporation of solvent ( ➲ precipitation / viscosity increase)
  - Corrosion, scaling from wall (➲ plugging of filter / nozzles)
  - Other contamination ("waste" / debris, mixing of dispersants etc.)
- **Norwegian regulations: re-checking every 3 year !**



## Rechecking of dispersants in stock

- Norwegian regulations: re-checking every 3 year ! (+ "internal control": Visual check every year)
- **Physical-chemical changes:**
  - Evaporation of solvent ( Gas Chromatography)
  - Visual evaluation: colour, precipitation
  - Viscosity / Density
- **Effectiveness:**
  - IFP test: 2/3 of the "original" dispersant performance



## *Basis for a rapid desion-making*

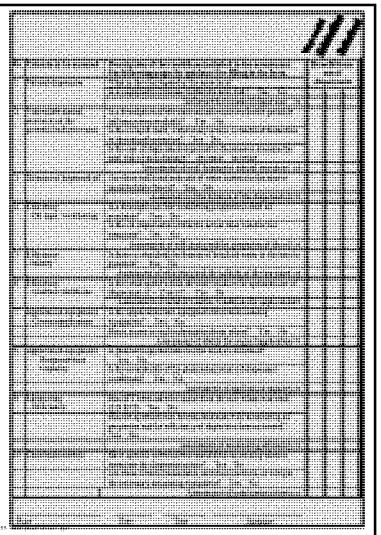
**What have to be documented in the <u>pre-approved plan:</u>**

- Natural resources / Sensitivity maps (seasonal)
- Degree of natural dispersion of the oil / "life-time" of the spill
- Potential effectiveness of dispersant treatment with respect to:
  - oil type / weathering degree
  - environmental conditions (weather, dilution, salinity etc.)
- Capacity of the application response method / application strategy
- Monitoring: measure the effectiveness / Criteria for when to stop spraying

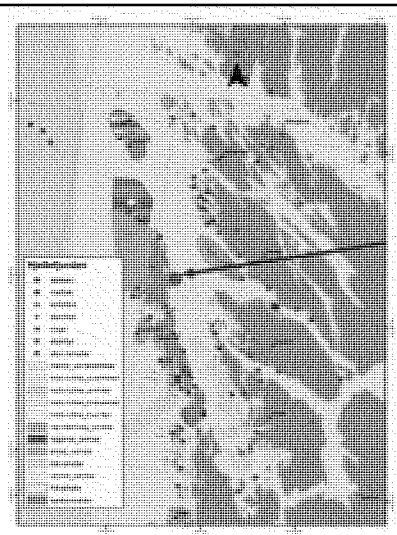
**<u>In a spill situation:</u> has to be filled out an operational "check-list" / report form:**

## Operational report form – a "check-list":

- Users "Internal control procedure" in a decision-making situation
- To ensure that decision to use dispersants is within the conditions as fundamented in the pre-approved contingency plans.
- Filled out by the user - within minutes!!
- The form is sent to the Norwegian Authorities when starting the dispersant spraying operation







## Natural resources around the

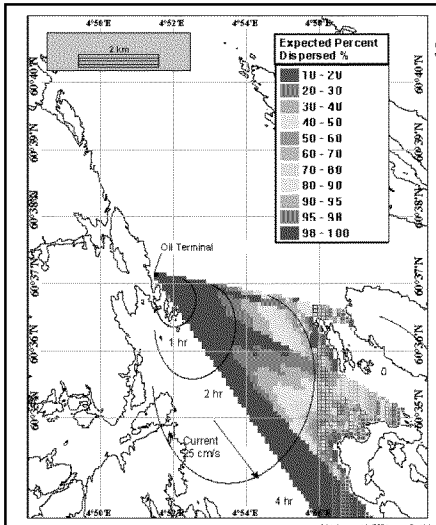
## Sture oil terminal

**Sensitivity maps based on:**

1. Marine Resource Data-Base (MRDB)
2. Priority of resources:
   - vulnerability
   - Concervational value

   "MOB" – index-system:
   6 categories: MOB A → F






**Sture oil terminal contingency plan**

## Areas for application of dispersants

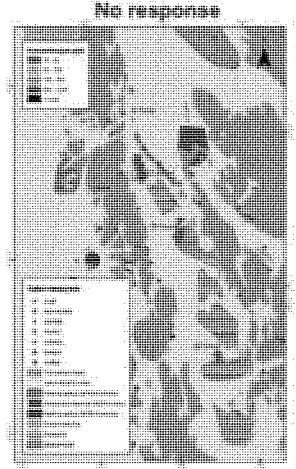
- **No specific minimum requirements to depth and distance from land**
- **Maps for different wind / current drifting directions**
- **If not, general guidance:**
  **Depth: > 20 m**
  **Distance: > 200 m**

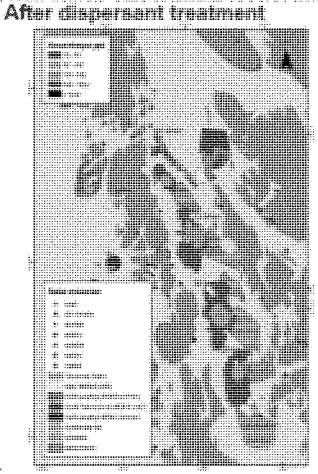


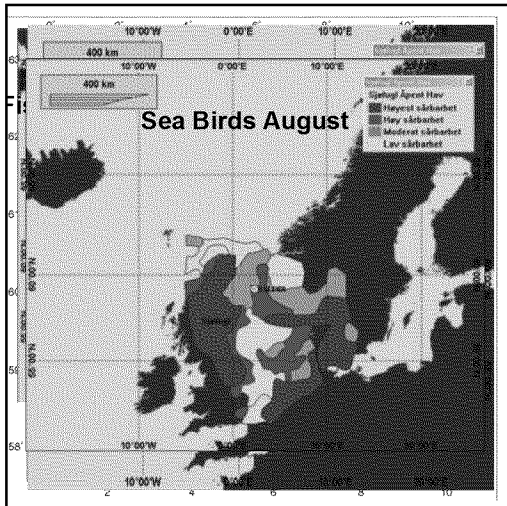
## Dilution rate of dispersed oil in the water column

Scenario: 3, 6 12, 18 and 24 hours after release, 100m³ from the Sture oil terminal (OSCAR-simulation)

**No response** **After dispersant treatment**








## Natural resources around the Balder oil field in the North Sea

Sensitivity map data-base



## Fish and bird activity at the Balder / Jotun field

Spawning periods:

| Species | Month 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cod | | | | | | | | | | | | |
| Haddock | | | | | | | | | | | | |
| Whiting | | | | | | | | | | | | |

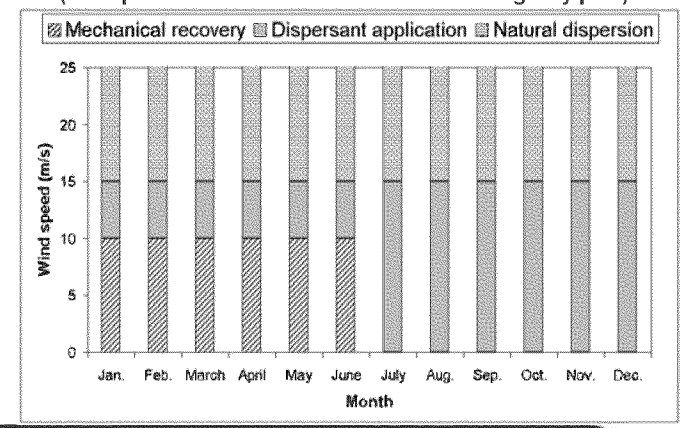
Sea bird life cycle periods:

| Activity | Month 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Breeding | | | | | | | | | | | | |
| Moulting | | | | | | | | | | | | |
| Migrating | | | | | | | | | | | | |



## "Strategy" for the initial oil spill response options at offshore installations

(Example taken from the Balder / Jotun contingency plan)



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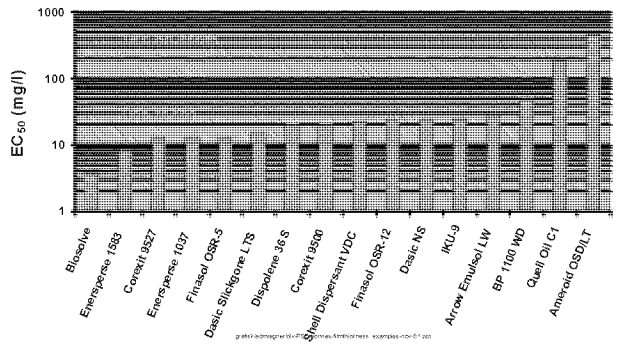




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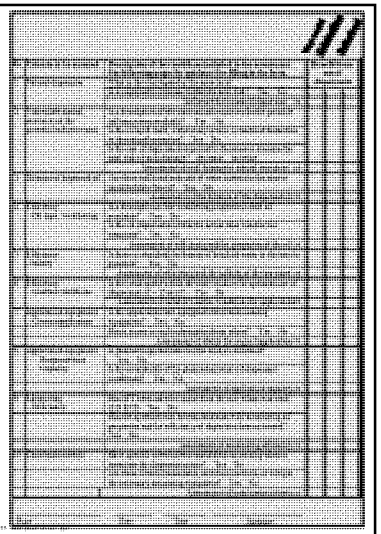



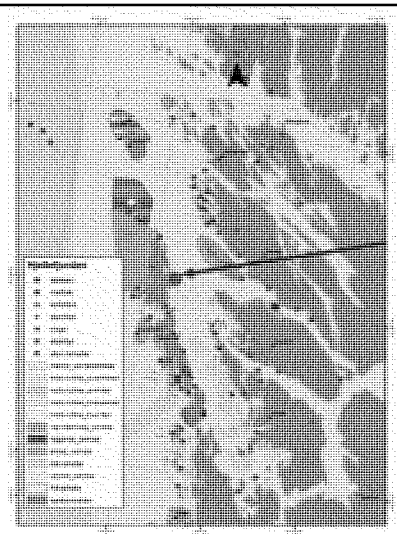

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## Sture oil terminal

**Sensitivity maps based on:**

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   "MOB" – index-system:
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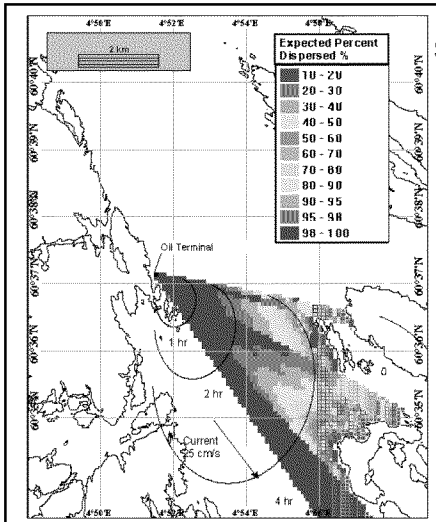



**Sture oil terminal contingency plan**

## Areas for application of dispersants

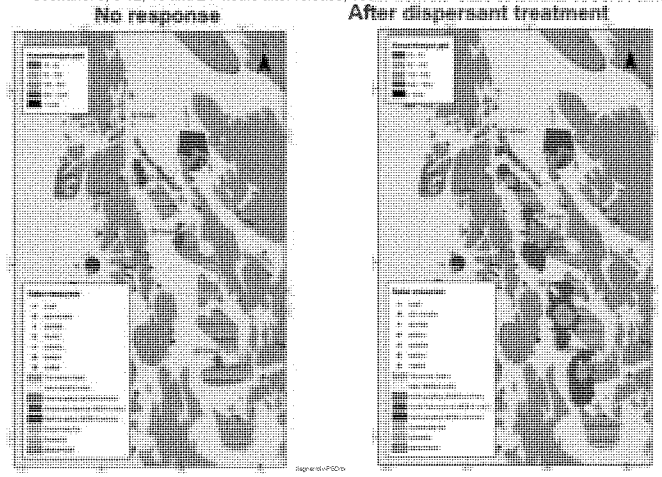
- **No specific minimum requirements to depth and distance from land**
- **Maps for different wind / current drifting directions**
- **If not, general guidance:**
  **Depth: > 20 m**
  **Distance: > 200 m**

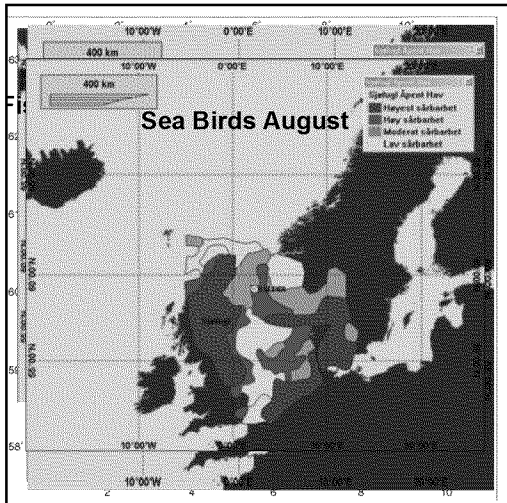


## Dilution rate of dispersed oil in the water column

Scenario: 3, 6 12, 18 and 24 hours after release, 100m³ from the Sture oil terminal (OSCAR-simulation)

**No response** | **After dispersant treatment**






## Natural resources around the Balder oil field in the North Sea

Sensitivity map data-base



## Fish and bird activity at the Balder / Jotun field

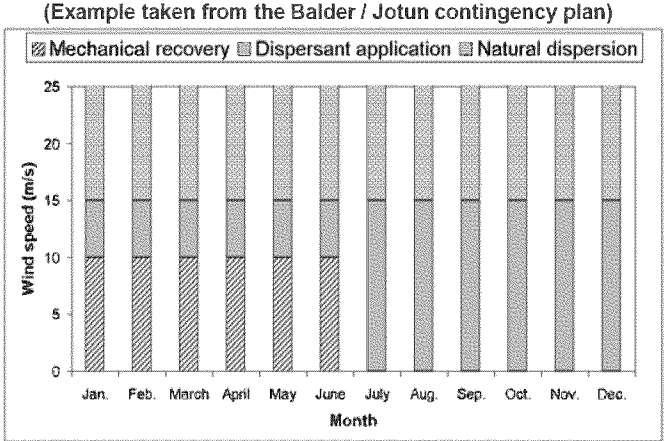
Spawning periods:

| Species | Month 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cod | | | | | | | | | | | | |
| Haddock | | | | | | | | | | | | |
| Whiting | | | | | | | | | | | | |

Sea bird life cycle periods:

| Activity | Month 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Breeding | | | | | | | | | | | | |
| Moulting | | | | | | | | | | | | |
| Migrating | | | | | | | | | | | | |



## "Strategy" for the initial oil spill response options at offshore installations

(Example taken from the Balder / Jotun contingency plan)