Monitoring Subsurface Oil released from Deepwater Horizon MC 252 in the Gulf of Mexico

Kenneth Lee

Centre for Offshore Oil, Gas and Energy Research (COOGER)

Fisheries and Oceans Canada

Ken.Lee@dfo-mpo.gc.ca

Fisheries and Oceans Canada | Pêches et Océans Canada

Centre for Offshore Oil, Gas and Energy Research (COOGER)

- Primary role is research to assess the risks from offshore oil and gas and ocean renewable energy activities and to develop of mitigation technologies
- Identification of R&D needs
- National coordination of regional expertise and infrastructure
- Provision of scientific support for decision making for policy and regulations
- Promote national / international research collaborations with other government agencies, industry and academia

Offshore Environmental Impacts

Assessment of environmental impacts and risks associated with exploration, production and transport operations

Primary program focus:

- **Drilling wastes**
- **Produced water**
- **Seismic impacts**
- **Assessment of oil spill impacts and remediation**

A balanced multidisciplinary research program that maintains expertise to enable response to future environmental issues

DFO Oil Spill Countermeasure Research

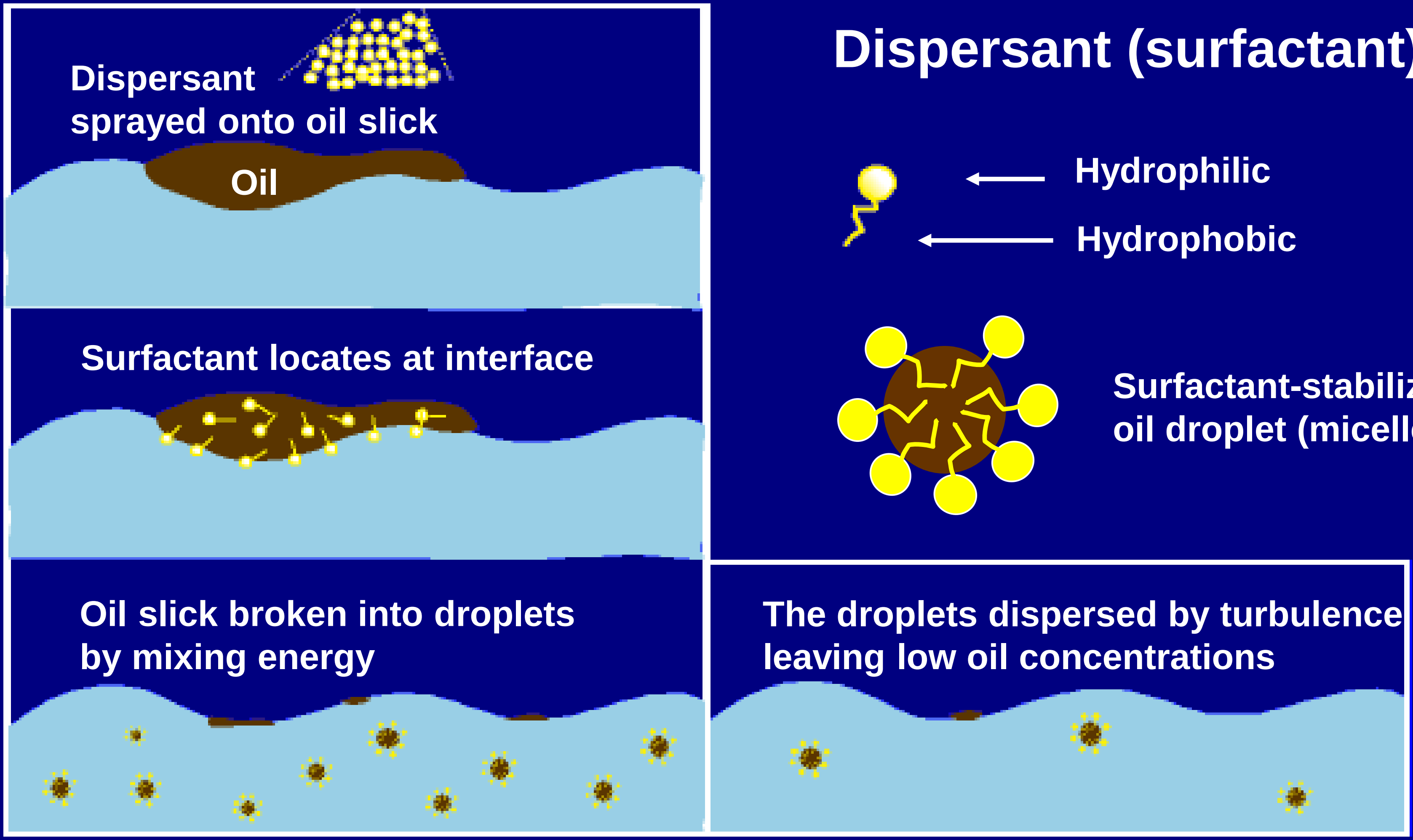
By the conduct of laboratory, mesocosm and "controlled oil spill" experiments in the field, DFO developed oil spill countermeasure technologies (bioremediation, phyto-remediation and surf-washing) and methodologies to quantify habitat recovery

Why Chemical Dispersants?

- There is no single response technique that is suitable for all circumstances
- Oil spill responses:
  - Booming and skimming
  - *In-situ* burning
  - Bioremediation
  - Chemical dispersion

- At open sea, dispersant use attracts most attention due to restrictions to other methods

Activity of Chemical Dispersants



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

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

Chemical Constituents (Dispersant – Corexit)

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

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

Enhanced Dispersion for Oil Spill Response

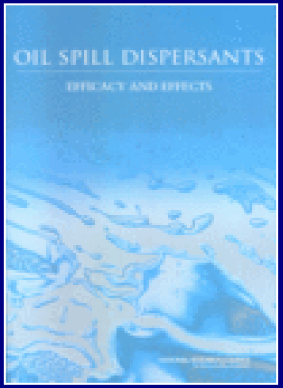
- Based on the concept of transferring oil from the sea surface into the water column, as small oil droplets
- These are diluted by natural processes to concentrations below toxicity threshold limits
- Dispersed oil droplets are degraded more rapidly by natural bacteria
- Achieved with chemical oil dispersants and/or facilitation of oil mineral aggregate formation

DFO Research Priorities

Uncertainties remain high regarding dispersant use at sea

- **Dispersant efficacy at different sea states is not clear**
- **Biological effects of dispersed oils are poorly understood**

National Research Council (NRC) Committee on Understanding Oil Spill Dispersants: Efficacy and Effects (2005) Identified two factors to be addressed in oil dispersant efficacy studies:



- **Energy dissipation rate (turbulence/sea state conditions)**
- **Particle size distribution and mass balance**

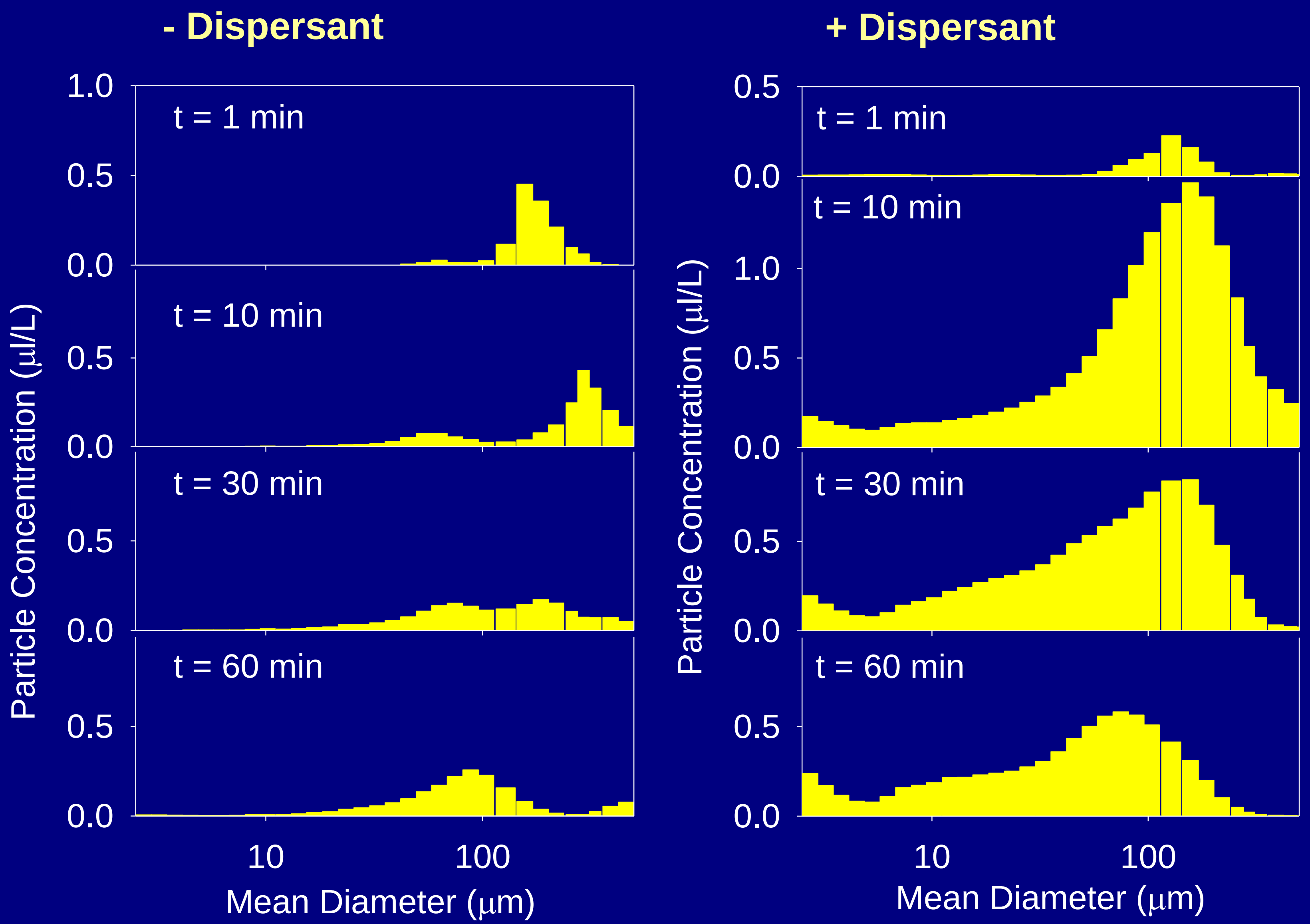
To address this issue, a wave tank facility was constructed by Fisheries and Oceans Canada (DFO) and the U.S. Environmental Protection Agency (EPA)

BIO Wave Tank

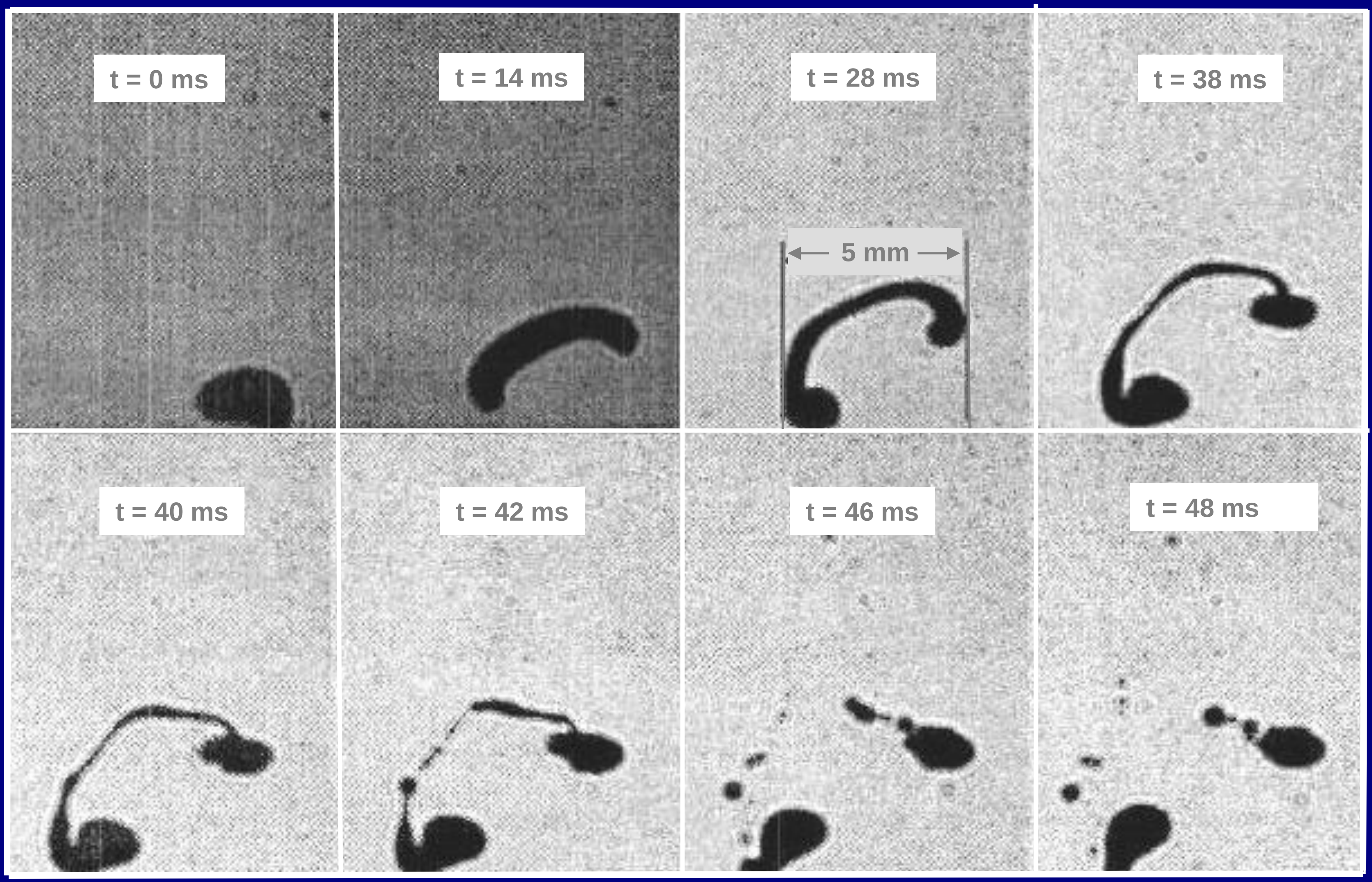
- Tidal current simulation by vertical manifolds along the sides of the tank
- Reproducible waves produced (of known energy dissipation rate), including breaking waves, at precise locations along length of tank
- Development of experimental protocols and instrumentation to monitor dispersed oil in the water column

Oil Droplet Size Distribution

LISST Particle Size Analysis



Dispersant Activity



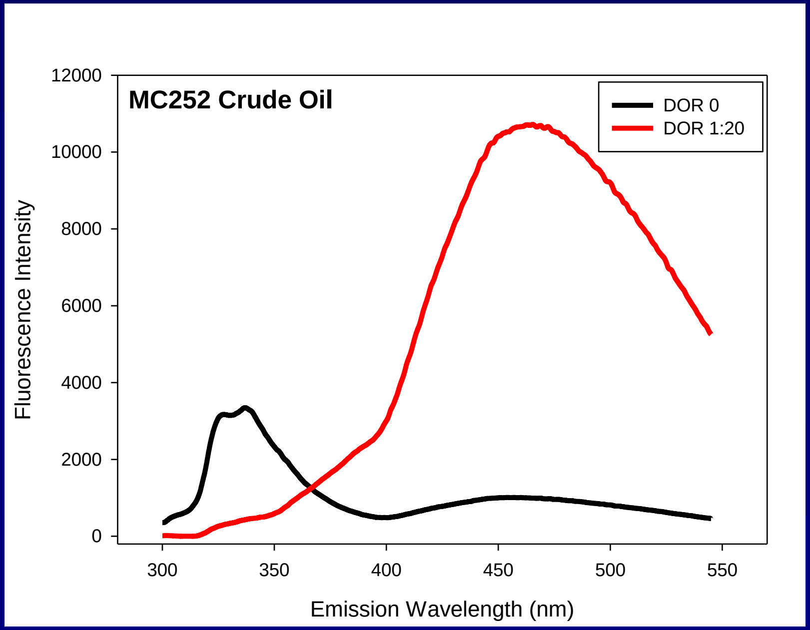
Extracted images from cinematic digital holography of turbulent break-up of crude oil mixed with dispersants into microdroplets

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

UV Fluorescence of Oil in Seawater

When a relatively high concentration of MC 252 crude oil (650ppm) is subject to UV excitation at 280nm:

- **Emission fluorescence is primarily located in a peak centered at 340nm in the absence of dispersant (DOR 0)**
- **Addition of Corexit 9500 at a DOR of 1:20 shifts emission to a large, broad peak centred at 450 nm**

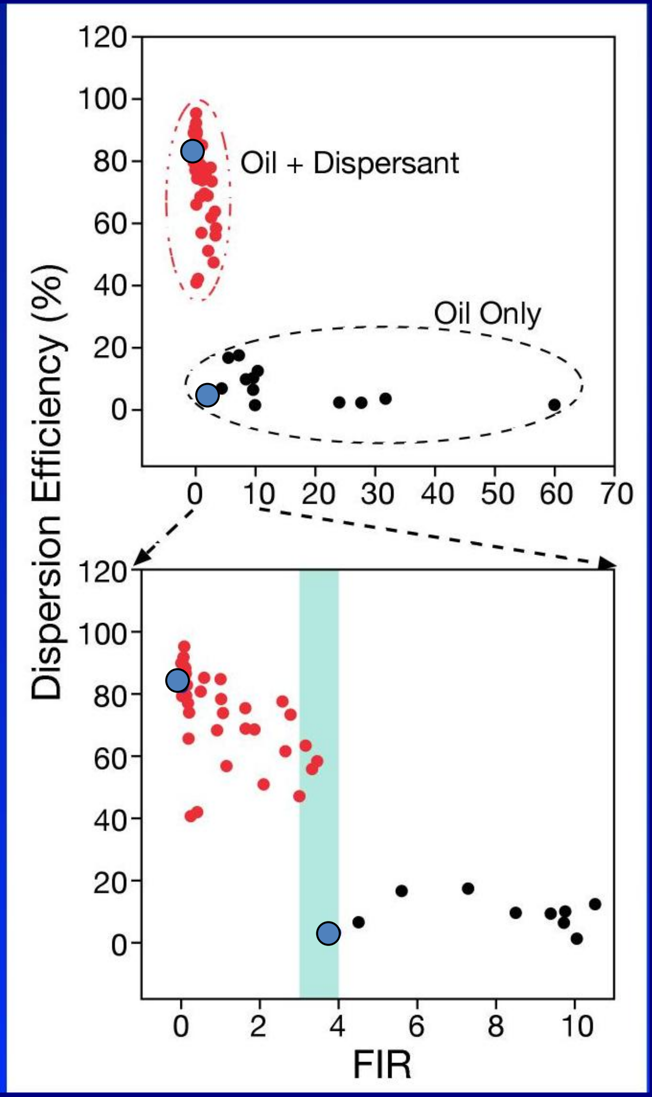


Fluorescence Intensity Ratio (FIR)

Emission at 340nm is divided by emission at 450nm

Oils dispersed on their own (with dispersion efficiencies of < 20%), were associated with FIRs > 4, while chemically dispersed oils (with efficiencies > 40%) were associated with FIRs < 4

FIR was a potential method to quickly assess whether an oil slick had been sufficiently dispersed (SMART Tier II)



Gulf of Mexico Oil Spill

Deepwater Horizon MC-252 oil spill - largest accidental marine oil spill in the history of the petroleum industry

- **April 20, 2010 – explosion on the Deepwater Horizon drilling rig killed 11 platform workers and injured 17 others**

- **July 15, 2010 - leak was stopped by capping the wellhead which had released 4.9 million barrels of crude oil**

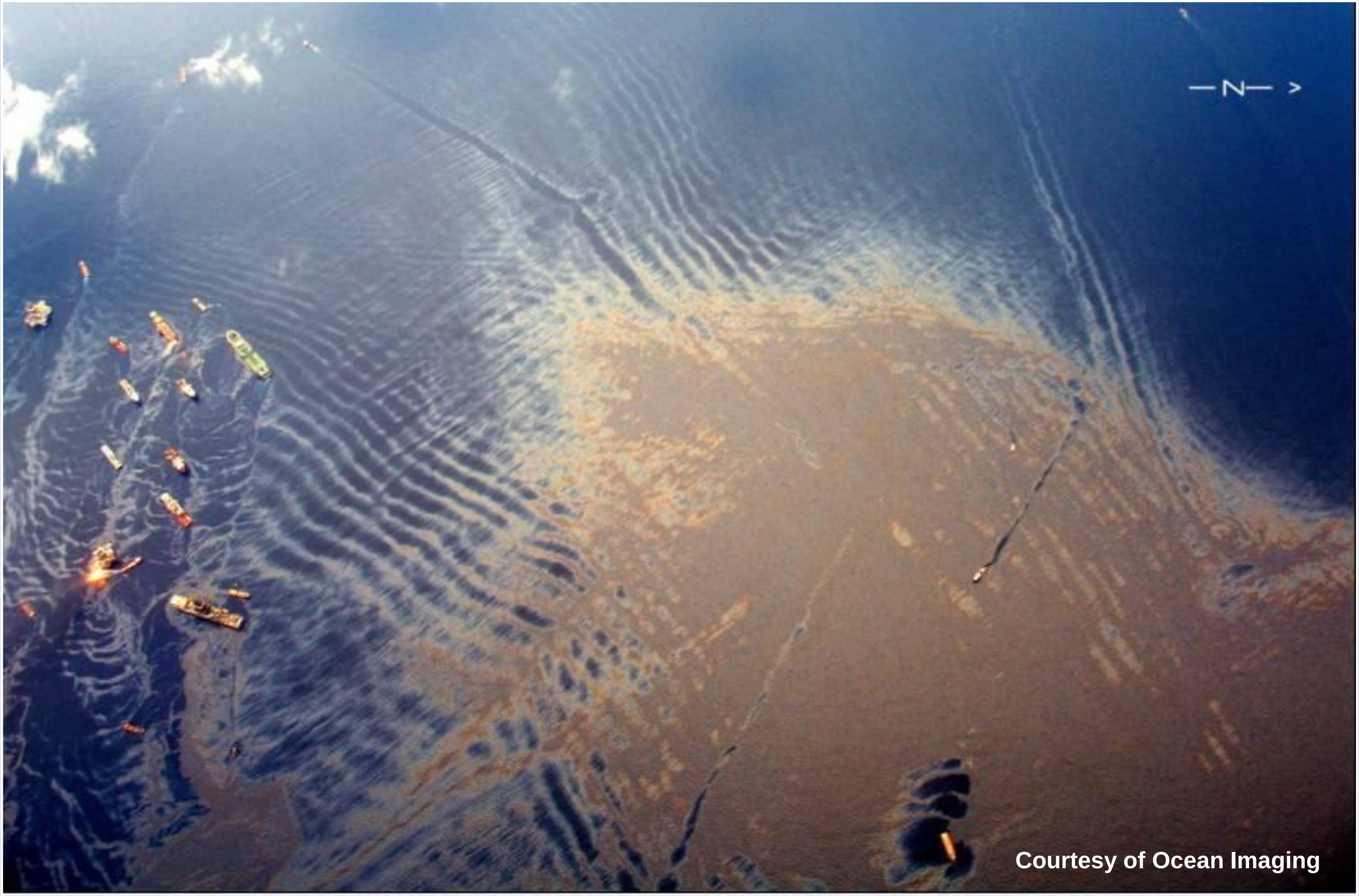
- **September 19, 2010 - federal government declared the well "effectively dead“ after successful completion of the relief well**

DWH Oil Spill Peak Statistics

- **4.9 million bbls of oil discharged**
- **1.8 million gallons of dispersants used**
- **411 in-situ burns conducted (265,450 bbls of oil burned)**
- **48,200 responders**
- **9,700 vessels (6,500 government owned)**
- **127 surveillance aircraft**
- **3.8 million ft of hard boom deployed**
- **9.7 million ft of soft boom deployed**

Gulf of Mexico – May 24, 2010

Encounter Rate is Key to Offshore Response



Courtesy of Ocean Imaging

Application of Oil Dispersants - GoM

- Based on discharge rates - final estimate of 53,000 barrels per day (8,400 m^3/d) - each day the Gulf of Mexico Oil Spill would be considered a major incident

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

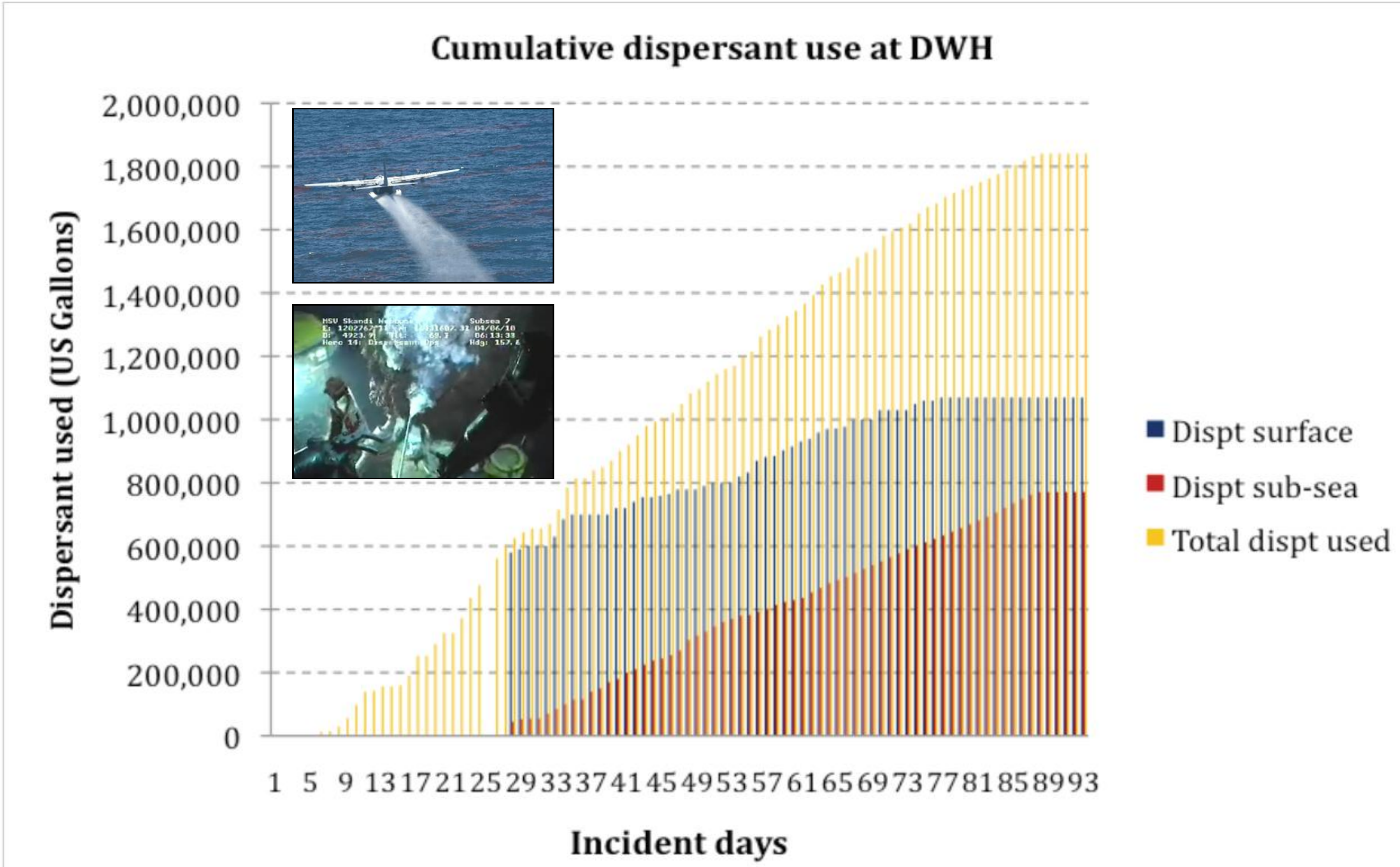
- Beginning in early May responders began injecting dispersants at the source of the release (~1500m depth) to reduce oil from reaching the surface
  - Advantages of subsurface injection:
    - Reduced VOCs (volatile organic compounds)
    - Reduced Oil Emulsification
    - Volume of dispersant needed

Dispersant Application on the Sea Surface

- Dispersant was applied from vessels by spraying when VOC levels near the source site reached unacceptable levels, enabling work to continue on the drilling and containment rigs/vessels

Subsurface Injection of Dispersants

Cumulative Dispersant Use



* 4,200,000 L of dispersant added by subsurface injection

Plume Monitoring and Assessment for Subsurface Dispersant Application
(US EPA Directive – May 10, 2010)

***PART 1*:** **“Proof of Concept”** to determine if subsurface dispersant operation is chemically dispersing the oil plume.

Following review by the RRT….

***PART 2*:** Robust sampling to **detect and delineate the dispersed plume** based on the results of PART 1 and input from hydrodynamic modeling

DFO COOGER was requested by US EPA to provide scientific expertise to implement the directive

All data provided to the United States Coast Guard (USCG)Federal On-Scene Coordinator, and the Environmental Protection Agency (EPA) Regional Response Team (RRT)

DFO Sampling Effort

	Person Days	Stations	Samples
May	91	68	1020
June	136	107	1674
July	136	65	1060
August	143	92	1439
Total	**506**	**320**	**5193**

* Cost recovery from the U.S. Government with BP as the responsible party accountable for all cleanup costs

R/V Ocean Veritas

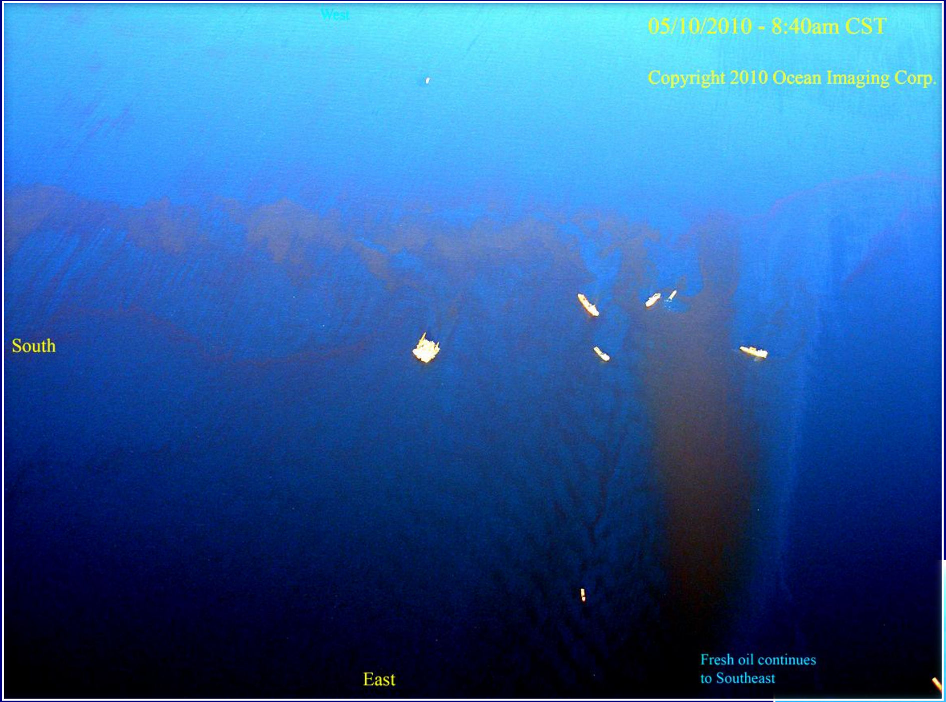

R/V Brooks McCall

Dispersant Monitoring and Assessment for Subsurface Dispersant Application

- US EPA and USCG directives required BP to implement a monitoring and assessment plan for subsurface and surface use of dispersants
  - Shutdown Criteria
    - Significant reduction in dissolved oxygen (< 2 mg/L)
    - Rotifer acute toxicity tests

- Later addenda to implement SMART Tier 3 Monitoring Program
  - Droplet size distribution (LISST)
  - CTD instrument equipped with CDOM fluorometer
  - Discreet sample collection to measure fluorometry (FIR)

* Aim to eliminate surface application altogether with subsea dispersant addition limited to < 15,000 gpd

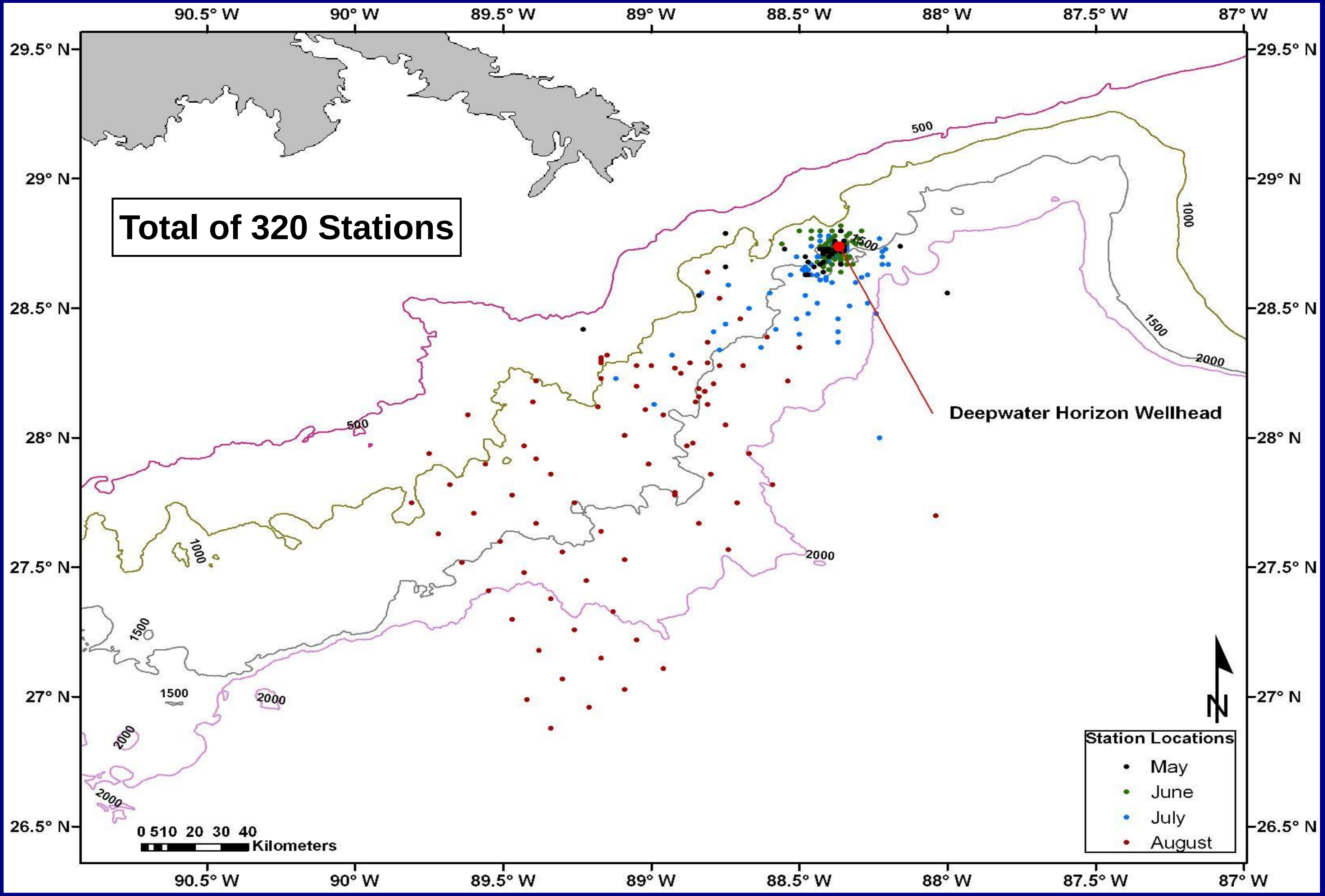

West
05/10/2010 - 8:40am CST
Copyright 2010 Ocean Imaging Corp.
South
East
Fresh oil continues
to Southeast

Joint Analysis Group (JAG)

Surface and Subsurface Oceanographic, Oil, and Dispersant Data

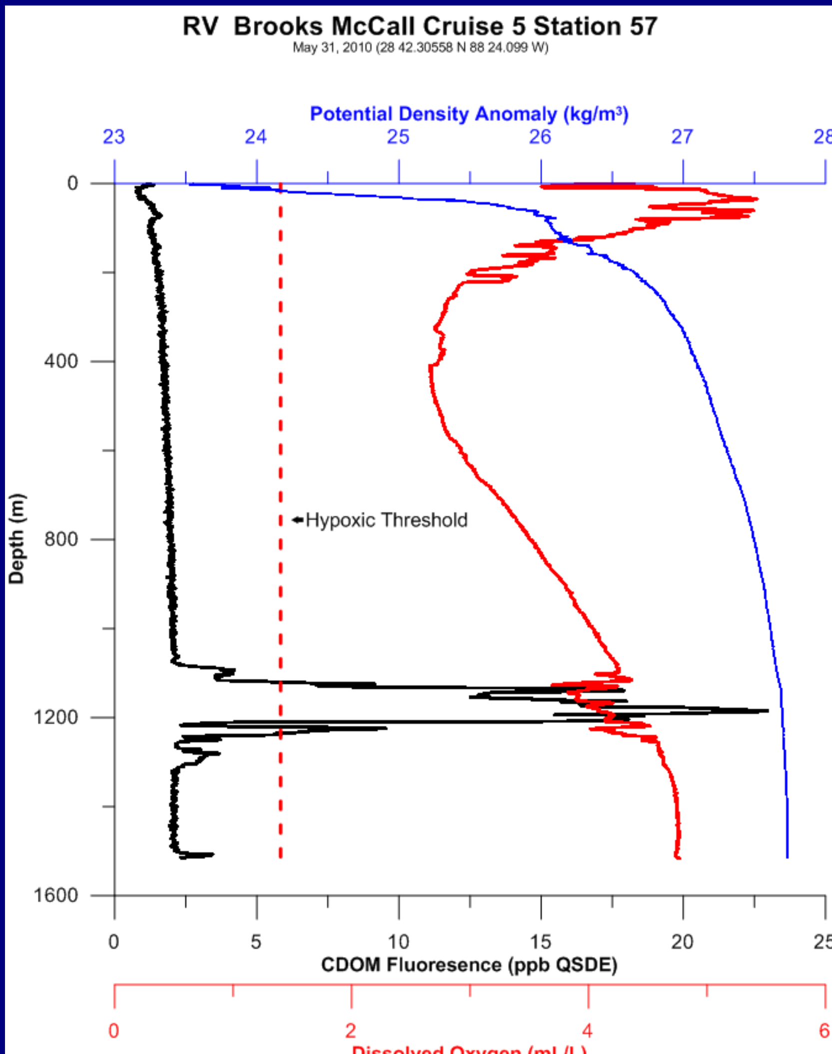
- Working group of scientists from EPA, NOAA, OSTP, BP and DFO
- Analyze an evolving database of sub-surface oceanographic data by BP, NOAA, and academic scientists
- Near term actions:
  - Integrate the data
  - Analyze the data to describe the distribution of oil and the oceanographic processes affecting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

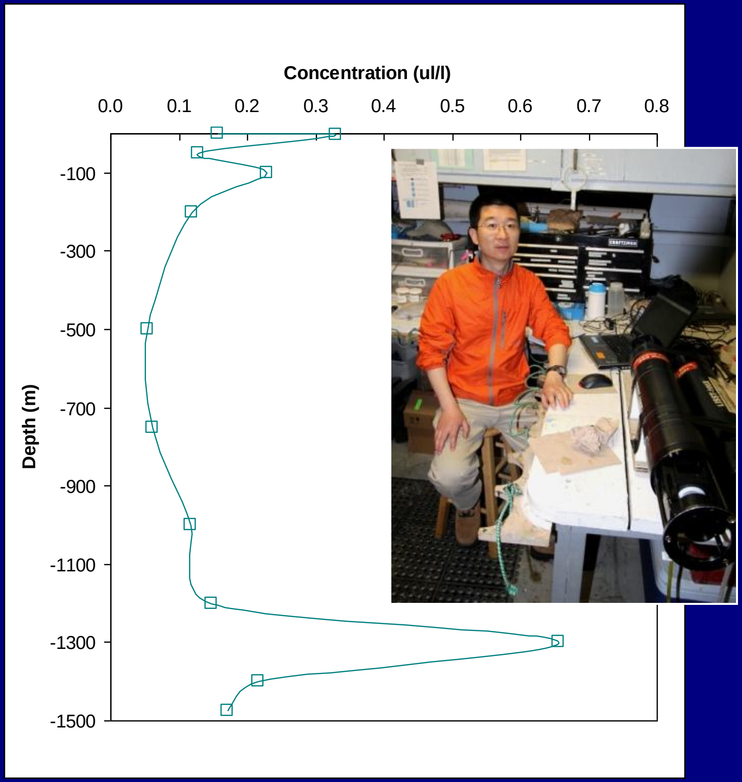
DFO Station Locations



Vertical Profile - DO_2 Depression

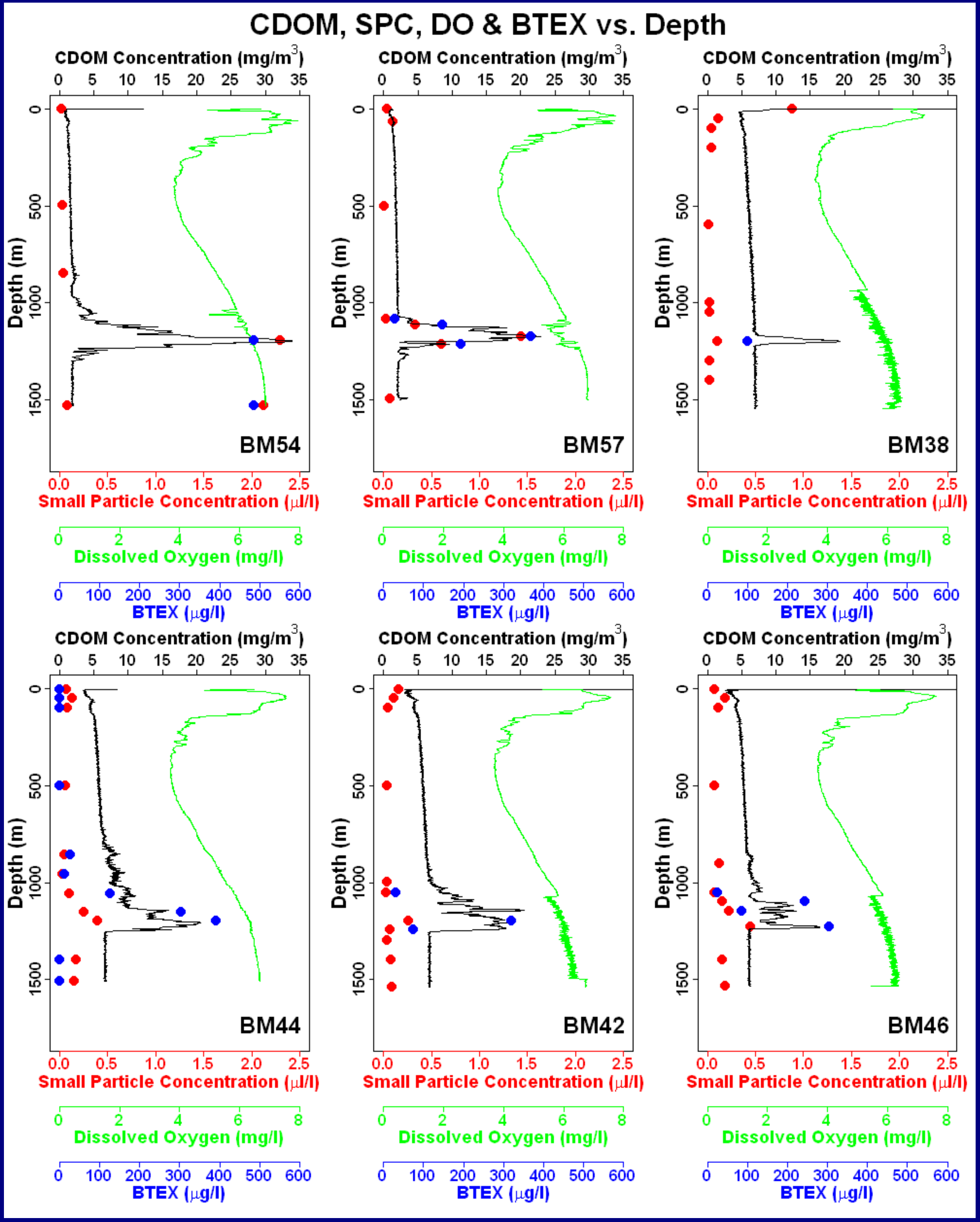
(coincident with fluorescence and <60µm LISST particle count peaks between 1100 and 1200 m)





Small particles (2.5 - 60µm) were indicative of oil droplets in the subsurface plume

Sub-surface Oil Profiles

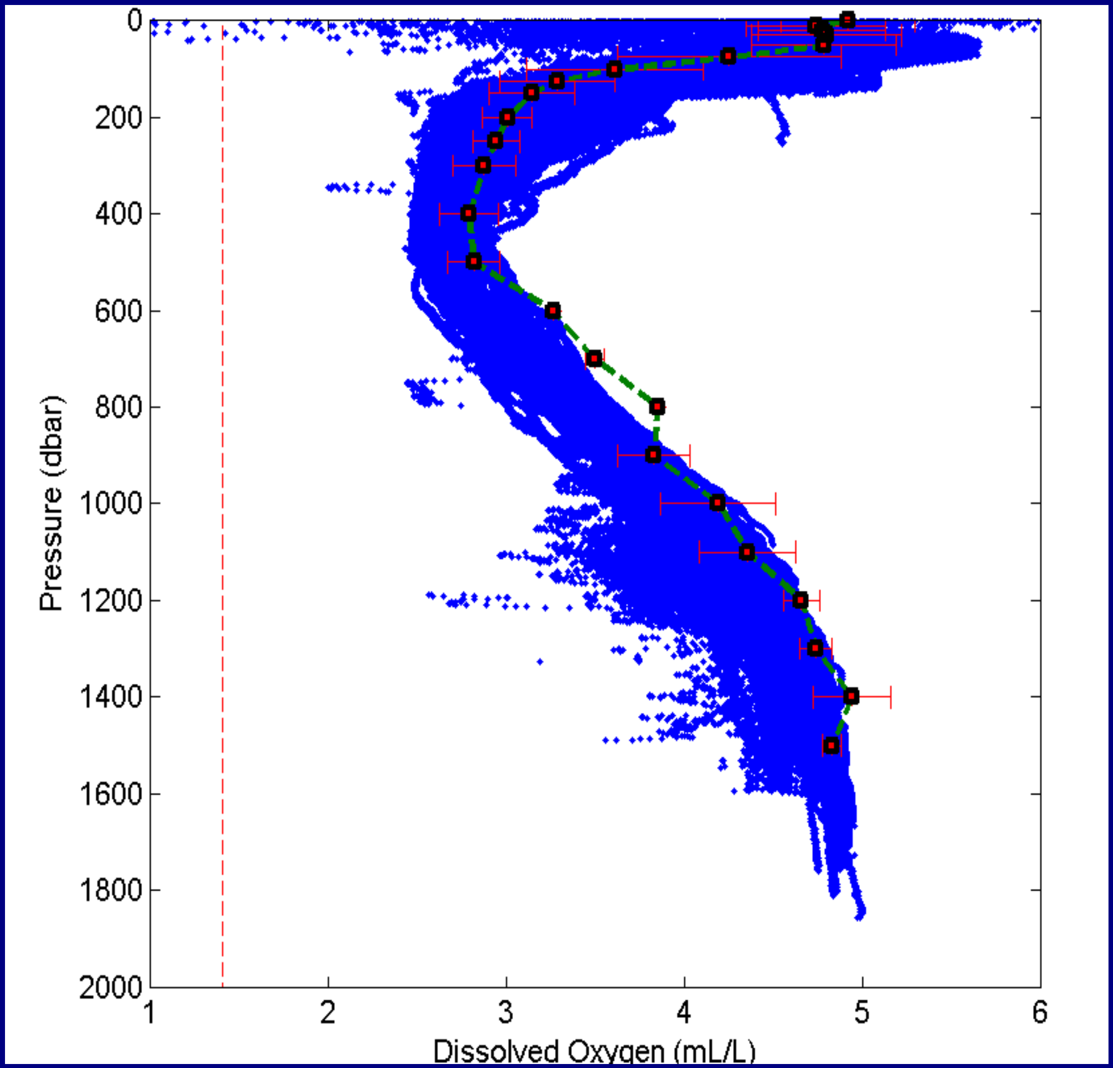


Oil Chemistry Results

All Depths						
	Number of Samples Analyzed			Summary of Samples >LOD (ppm)		
	Total	<LOD	>LOD	Min	Max	Median
BTEX	2743	2350 (86%)	393 (14%)	0.000144	0.4849	0.0121
PAHs	2307	1734 (75%)	573 (25%)	0.00002	10075.341	0.000188
nAlkanes	2304	2091 (91%)	213 (9%)	0.0005	23101.904	0.00068
Bottom (>700m)						
	Number of Samples Analyzed			Summary of Samples >LOD (ppm)		
	Total	<LOD	>LOD	Min	Max	Median
BTEX	1478	1164 (79%)	314 (21%)	0.00052	0.4849	0.027165
PAHs	1219	995 (82%)	224 (18%)	0.00002	0.0272	0.0001997
nAlkanes	1219	1104 (91%)	115 (9%)	0.0005	0.1357	0.00066

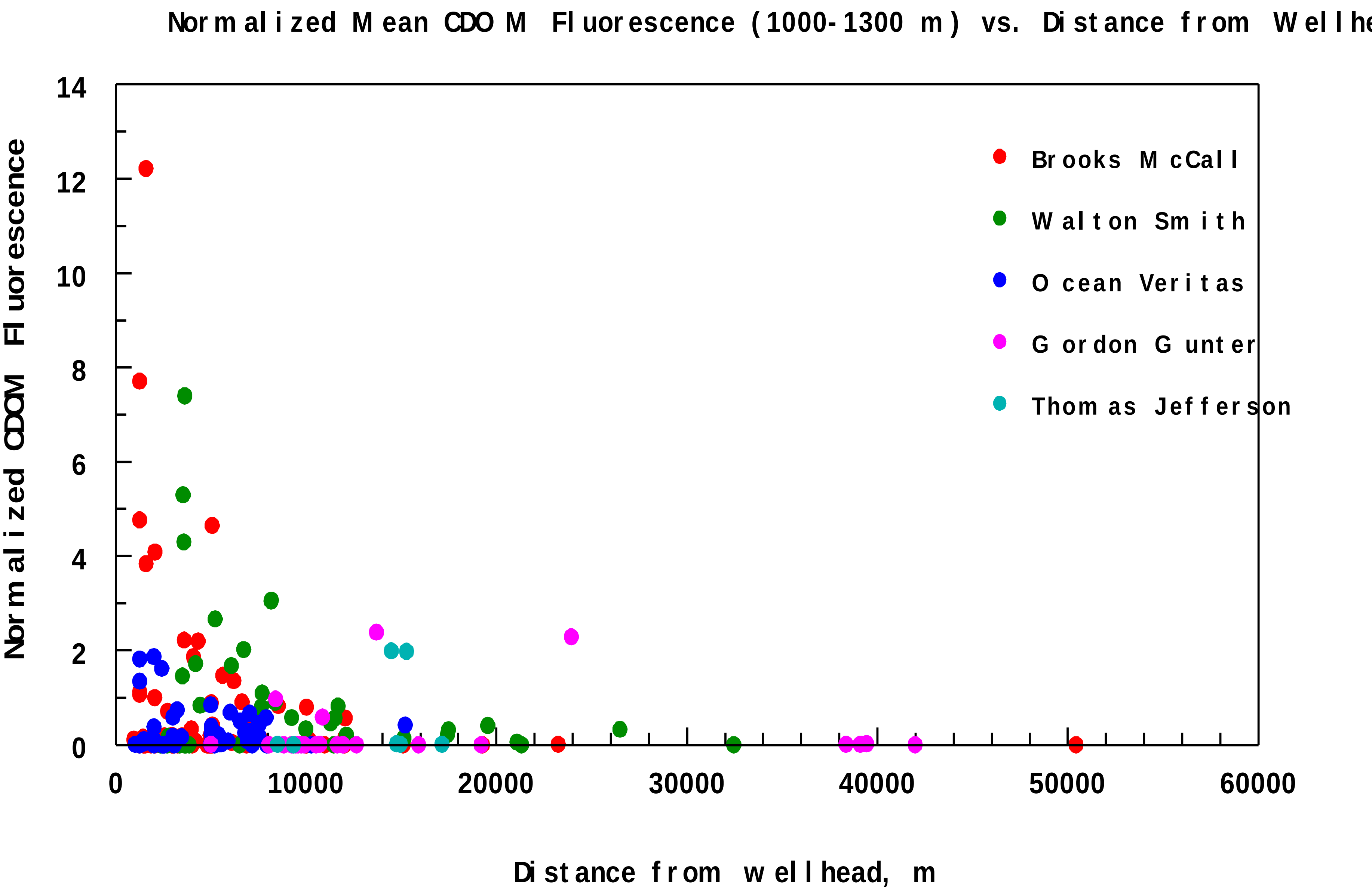


Level and Trend in DO_2 Depressions



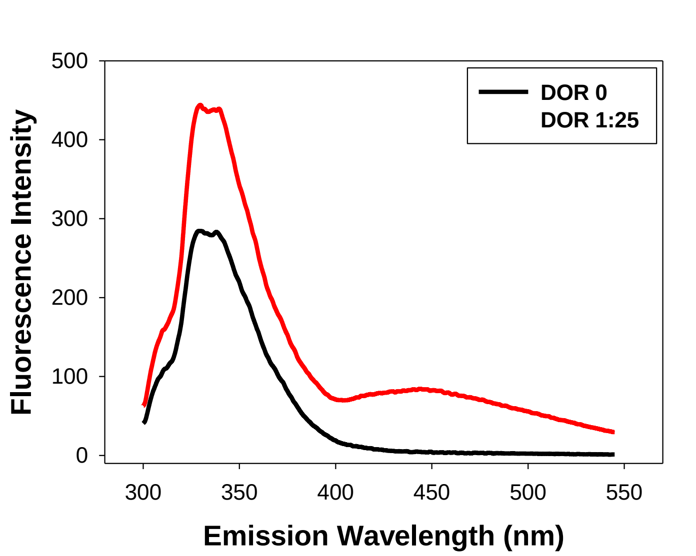
Total of 419 DO_2 profiles compared to annual mean climatology

CDOM (Colored Dissolved Organic Matter Fluorescence)



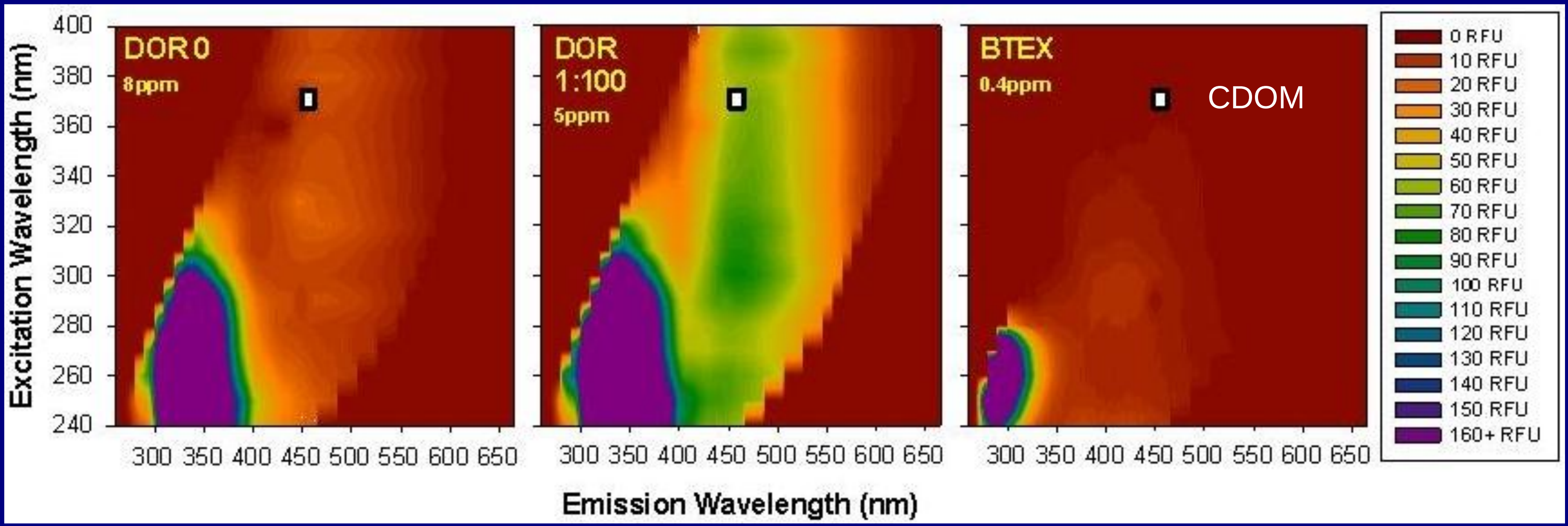
UV Fluorescence Analysis

- FIR only applicable at high oil concentrations (100's of ppm)
  - Gulf of Mexico water samples were much lower (low ppm to ppb range)
- UV fluorescence can detect low concentrations of oil (excitation: 280nm / emission 340nm)
- Many of the fluorometers deployed during the Deepwater Horizon spill employed higher excitation and emission wavelengths
  - Instruments should be modified to lower wavelengths for detection of dispersed oil at low concentrations



DFO – NOAA Workshop

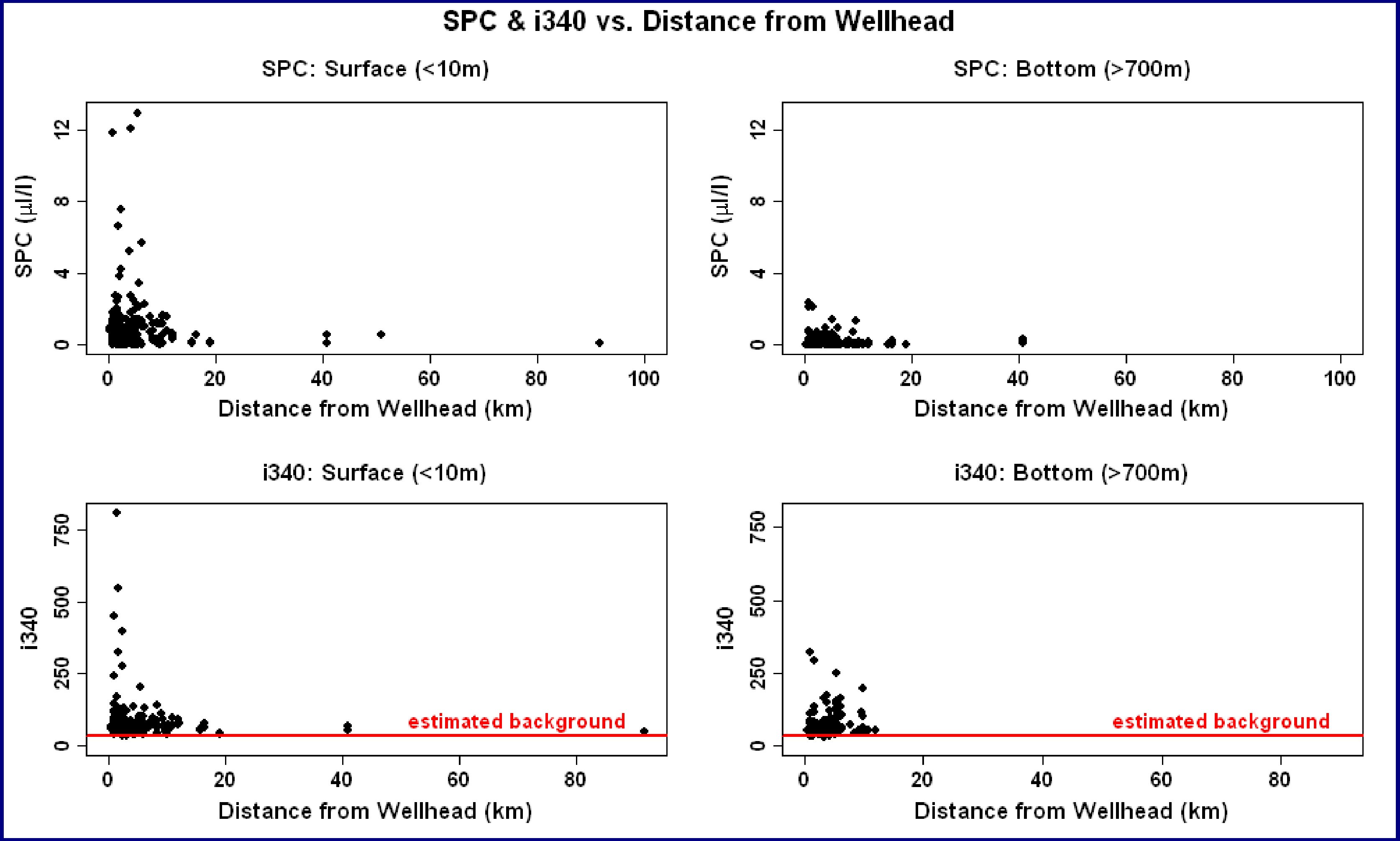
3D Fluorescence Spectra: MC252 & BTEX



DFO/NOAA Fluorometry Workshop

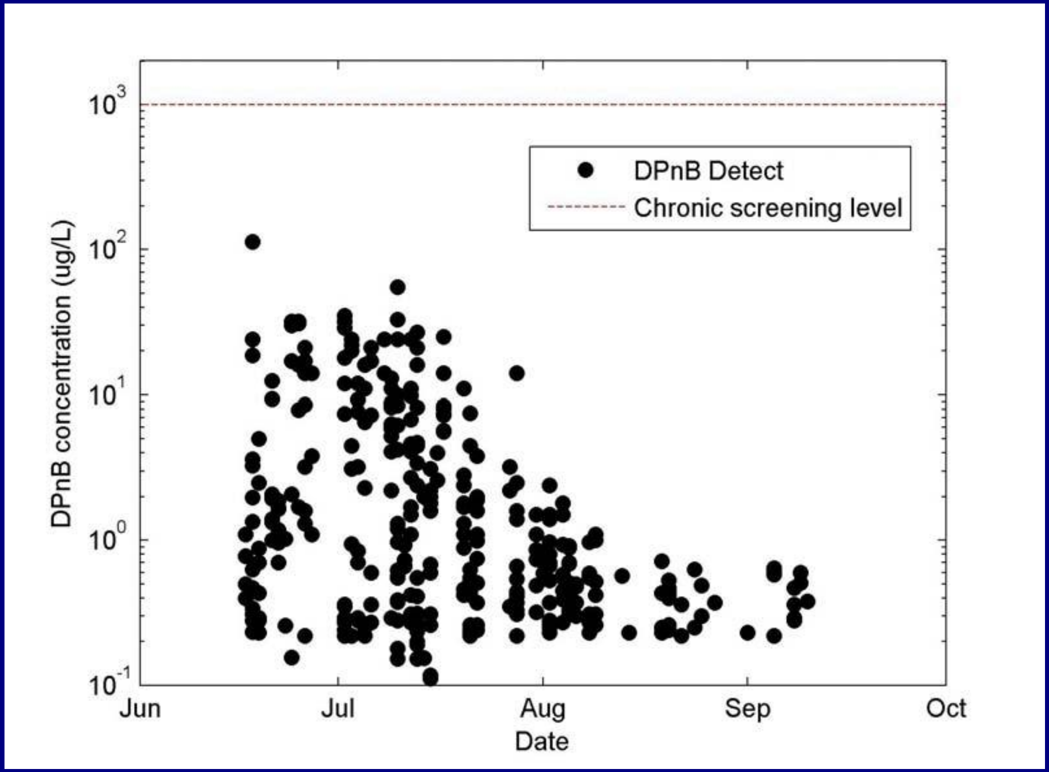
- Chelsea Aquatrack
- Wetlabs Safire
- Wetlabs Eco
- Wetlabs EcoTriplet
- Turner C7
- Satlantic Suna

UV-Fluorescence



Corexit Tracer

2-butoxyethanol, dipropylene glycol n-butyl ether (DPnB) was used to determine the expanse of the Deepwater Horizon dispersed oil and Corexit



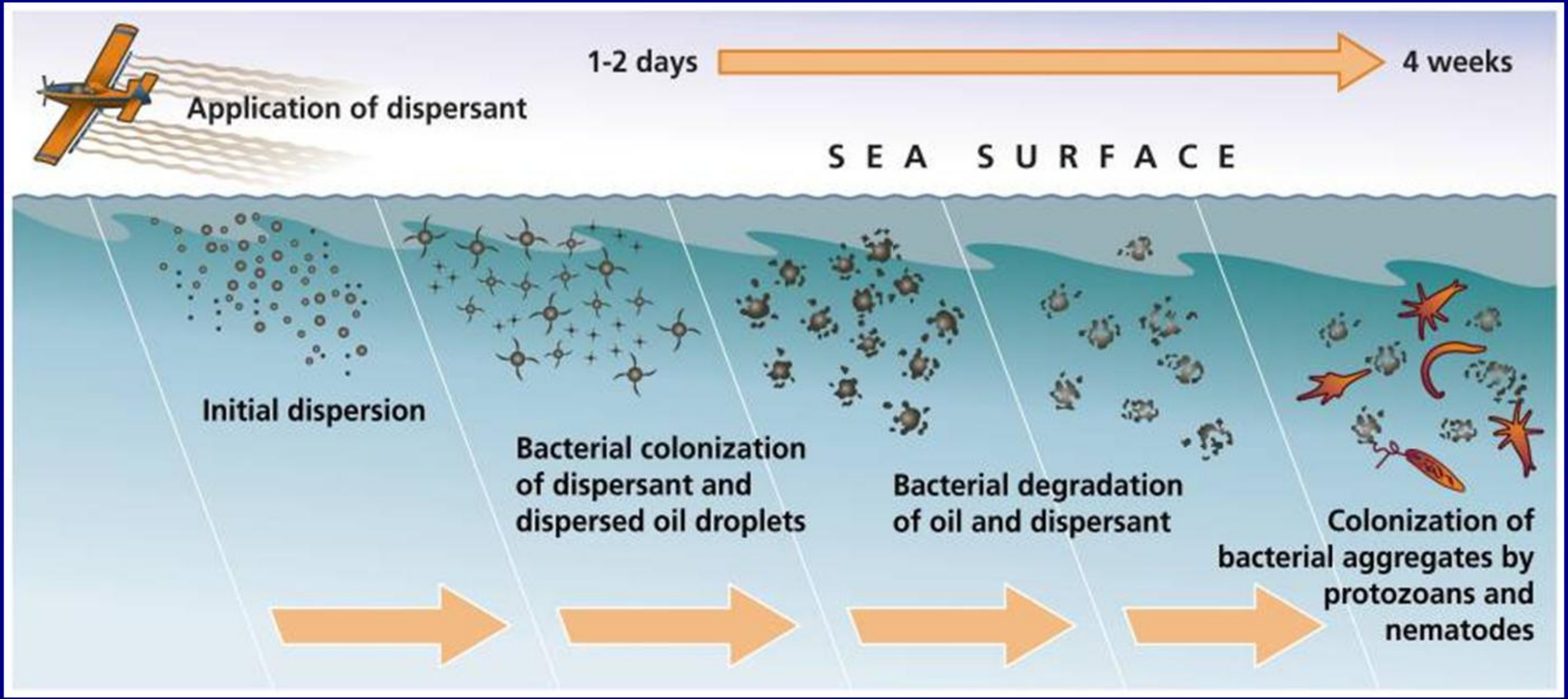
Operational Science Advisory Team:

Summary Report for Sub-sea and Sub-surface Oil and Dispersant Detection: Sampling and Monitoring, *Summary Report for Sub-sea and Sub-surface Oil and Dispersant Detection: Sampling and Monitoring*.

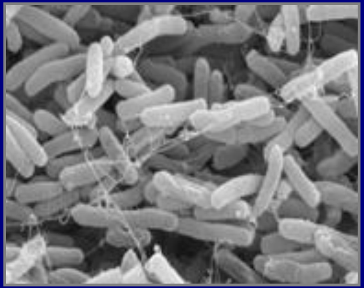
Unified Area Command, New Orleans, LA, 2010.

* USEPA chronic screening level = 1,000 µg/L

Fate of Dispersed Oil Droplets



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



Analysis of Near-field Oil Droplet Data

(JAG Analysis DFO Data: Dr. J.A. Galt, NOAA, HAZMAT)

- Within 15 km of the well and below 1000 m oil droplet concentrations (< 65 microns) were fully consistent with an essentially neutrally buoyant plume

- The plume was filamentous, a significant fraction of the bottle casts missed it and thus exhibited little or no oil in droplet form. Significant non-zero sample results, assumed to be within the filaments, showed total droplet volumes in the 10 ppm range with a max observed value of 16 ppm

- Observed values appeared to drop off by an order of magnitude within 10 km. If we use this as a rough scaling distance for the mixing and dilution of the oil droplet filaments or plume then we would expect to have total droplet concentrations reduced to the ppb level within about 40 km

- Although this is a rough estimate it is consistent with the bulk of the available observations and by the time the droplets get 40 kilometers away numerous other physical and biological processes will start to alter the state and composition of the plume

Fate of the Oil: GOM spill

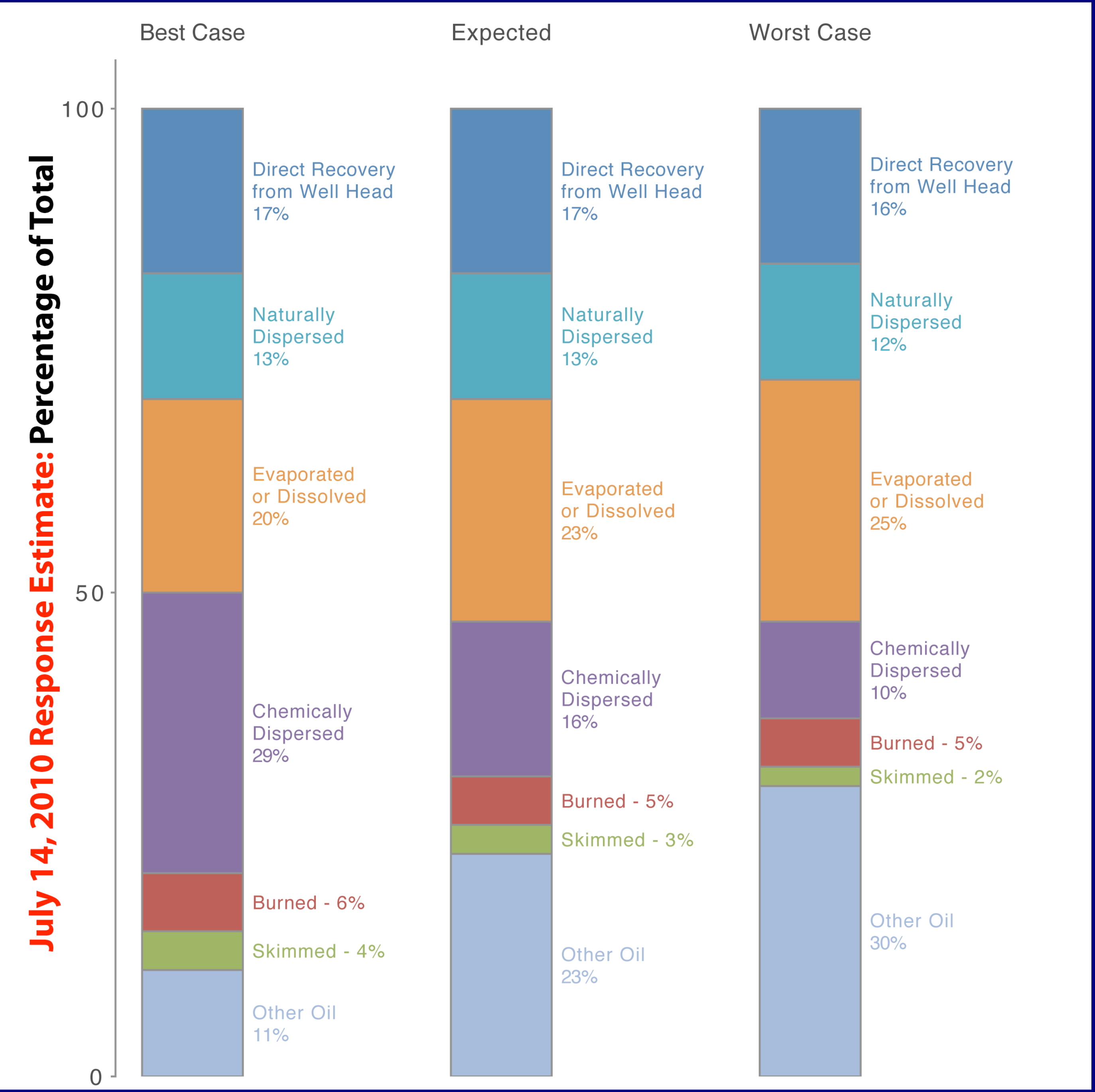
Response estimates expressed as % cumulative volume of oil discharged in the best, expected, and worst cases

Oil Budget Calculator

October 2010

NOAA (National Oceanic and Atmospheric Administration)

Other: Remaining oil is at the surface as light sheen or weathered tar balls, biodegraded, or already came ashore



Future of Dispersant Use

- The ability to effectively deploy and monitor an unprecedented dispersant response in the GoM was based on the past decades' improvements

- Misperceptions and knowledge gaps over their use remain Areas for improvement include:

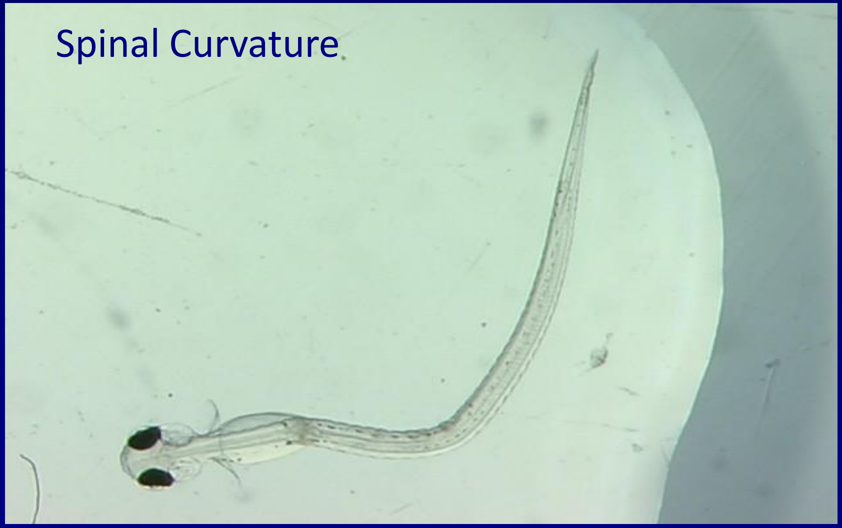
    - Need to be a common understanding of the risks and benefits of dispersant use, as well as the safety and effectiveness of dispersant products

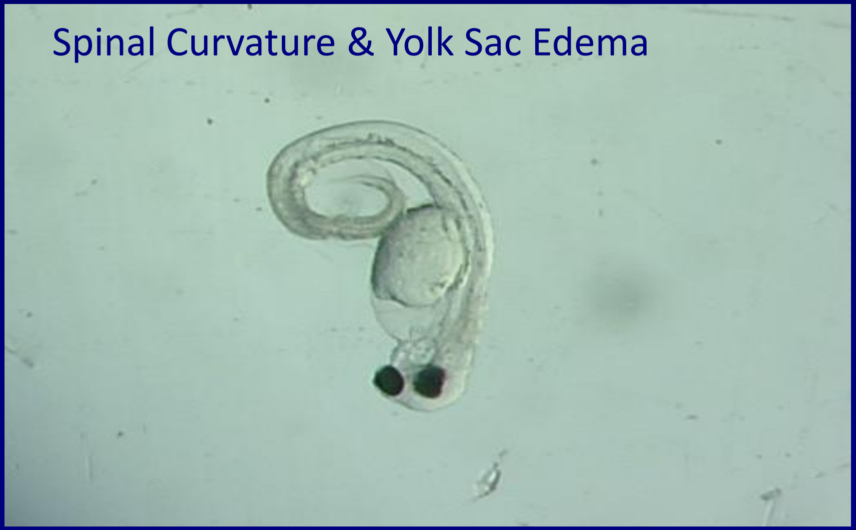
    - Additional research is needed on the behavior and long term fate of dispersed oil in the water column when dispersants are applied at the sea floor

    - Conduct of field trials to advance and validate existing knowledge

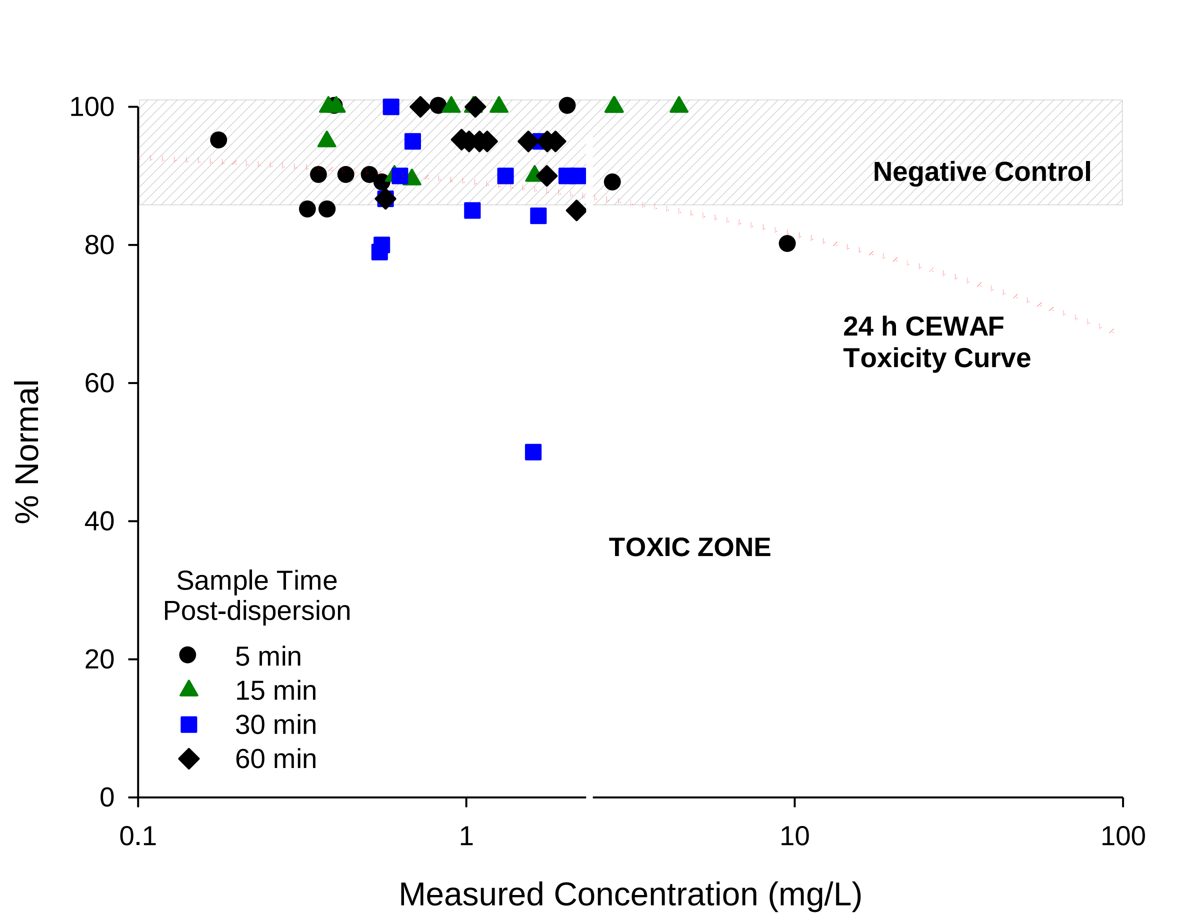
- Revision of IMO Guidelines for Chemical Oil Dispersant Use

Toxicity of Dispersants





Wave tank Toxicity Studies



Hydrocarbon concentrations for Arabian light crude oil were not high enough to cause toxicity in Atlantic herring embryos

GoM Spill Related Publications 2010-2011

Accepted (In Press):

Lee, K, Z. Li, P. Kepkay and S. Ryan (2011) Measurement of Concentration and Size Distribution of Surface and Subsurface Small Particles Using LISST-100X at the Deepwater Horizon Spill Site. Joint Analysis Group (JAG) Technical Report, Unified Area Command. 86pp.

Niu, H., Li, Z., Lee, K., Kepkay, P. Mullin J. (2011). Study the transport of oil-mineral-aggregates (OMAs) in marine environment and assessment of their potential risks to benthic organisms. International Journal of Environment and Waste Management. Manuscript ID is IJEWM-12052. <u>In Press</u>.

Li, Z., Lee, K., King, T., Niu, H, Boufadel, M.C., and Venosa, A.D. Application of entropy analysis of in situ droplet-size spectra in evaluation of oil dispersion efficiency. Marine Pollution Bulletin (Accepted)

Niu, H., Li, Z., Lee, K., Reed, M, and Mullin, J.V. 2011. Modeling oil spill from deepwater blowouts: Sensitivity of model to oil droplet size distribution. Marine Pollution Bulletin. Manuscript ID MPB-D-11-00204. (Accepted)

Published:

Wanh, W., Y. Zheng, Z. Li and K.Lee (2011) PIV investigation of oil–mineral interaction for an oil spill application. Chemical Engineering Journal 170: 241-249.

Lee, K., Z. Li, P. Kepkay and S, Ryan (2011) Time-series Monitoring the Subsurface Oil Plume released from Deepwater Horizon MC252 in the Gulf of Mexico. In: Proceedings of the International Oil Spill Conference (IOSC 2011), Portland, Oregon, USA. May 23 – 26, 2011. Paper #:2011- 381.

Lee, K., Z. Li, B. Robinson, P. Kepkay, M. Blouin and B. Doyon (2011) Field trials of in-situ oil spill countermeasures in ice-infested waters. In: Proceedings of the International Oil Spill Conference (IOSC 2011), Portland, Oregon, USA. May 23 – 26, 2011. Paper #: 2011-160

Lee, K., T. Nedwed and R. Prince (2011) Lab tests on the biodegradation rates of chemically dispersed oil must consider natural dilution. In: Proceedings of the International Oil Spill Conference (IOSC 2011), Portland, Oregon, USA. May 23 – 26, 2011. Paper #:2011-245

Niu, H., Z. Li, P. Kepkay, K. Lee and J. Mullin (2011) Modeling the long term fate of oil-mineral-aggregates (OMAs) in the marine environment and assessment of their potential risks. In: Proceedings of the International Oil Spill Conference (IOSC 2011), Portland, Oregon, USA. May 23 – 26, 2011. Paper #: 2011-170

Li, Z., K. Lee, P. Kepkay, O. Mikkelsen and C. Pottsmith (2011) Niu, H., Z. Li, P. Kepkay, K. Lee and J. Mullin (2011) Monitoring dispersed oil droplet size distribution at the Gulf of Mexico Deepwater Horizon spill site. In: Proceedings of the International Oil Spill Conference (IOSC 2011) Portland, Oregon, USA. May 23 – 26, 2011. Paper #:2011-377

Lee, K., T. King, B. Robinson, Z. Li, L. Burridge, M. Lyons, D. Wong, K. Mackeigan, P. Hodson, S. Courtenay, S. Johnson and A. Venosa (2011) Toxicity effects of chemically-dispersed crude oil on fish. In: Proceedings of the International Oil Spill Conference (IOSC 2011) Portland, Oregon, USA. May 23 – 26, 2011. Paper #:2011-163

Lyons, M.C., D.K.H. Wong, I. Mulder, K. Lee and L.E. Burridge (2011) The influence of water temperature on induced liver EROD activity in Atlantic cod (*Gadus morhua*) exposed to crude oil and oil dispersants. Ecotoxicology and Environmental Safety 74: 904–910.

Niu, H., Li, Z., Lee, K., Kepkay, P. Mullin J., (2011) Sensitivity of a deepwater blowout model on oil droplet size distribution. In: Proceedings of the 34th AMOP Technical Seminar on Environmental Contamination and Response, Oct 4-6, 2011, Banff, Canada.

Niu, H., Li, Z., Lee, K., Kepkay, P.E., and Mullin, J.V. 2011. Modeling transport of oil-mineral-aggregates in marine environments and assessment of their potential risks. Environmental Modeling and Assessment, 16: 61-75, DOI: 10.1007/s10666-010-9228-0.

Boufadel, M.C., Y. Sharifi, B. Van Aken, B.A. Wrenn and K. Lee (2010) Nutrient and oxygen concentrations within the sediments of an Alaskan beach polluted with the Exxon Valdez oil spill. Environmental Science and Technology 44: 7418-7424.

Li, Z., Lee, K., King, T., Venosa, A.D. 2010. Effects of temperature and wave conditions on chemical dispersion efficacy of heavy fuel oil in an experimental flow-through wave tank. Marine Pollution Bulletin, 60: 1550 - 1559

Li, Z., B.A. Wrenn, B. Mukherjee, K. Lee, and A.D. Venosa (2010) Impacts of iron, nutrients, and mineral fines on anaerobic biodegradation of canola oil in freshwater sediments. Soil & Sediment Contamination 19: 244-259.

Niu, H., Li, Z., Lee, K., Kepkay, P., Mullin J.M. (2010), A Method for Assessing Environmental Risks of Oil-Mineral-Aggregate to Benthic Organisms. Human and Ecological Risk Assessment, Vol. 16, No.4, pp.762-782.

Niu, H., Li, Z., Lee, K., Kepkay, P. Mullin J., (2010) The Effects of Waves and Currents on the Transport of Oil-Mineral-Aggregates (OMAs) and their Potential Risks to Benthic Organisms. In: Proceedings of the 33nd AMOP Technical Seminar on Environmental Contamination and Response, June 7-9, 2010, Halifax, NS, Canada, pp.623-634. (EI).

Zhang, H., M. Khatibi, Y. Zheng, K. Lee, Z. Li, J.V. Mullin (2010) Investigation of OMA Formation and the Effect of Minerals. Marine Pollution Bulletin 60: 1433-1441.