Fluorescence-Based Detection of Oil and Oil-Dispersant Mixtures in Seawater

Deepwater Horizon Oil Spill

Principal Investigator One Year Update Workshop

St. Petersburg, Florida

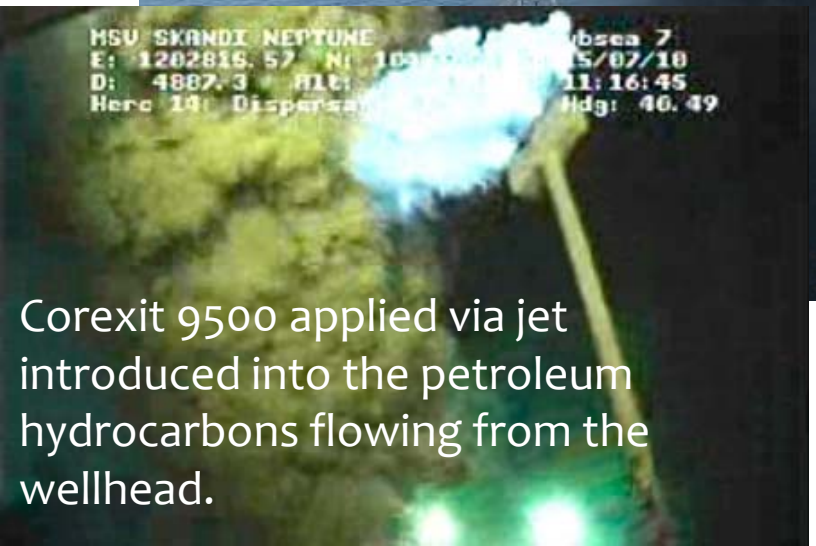
25 October 2011

Mary I. Abercrombie, USF College of Marine Science

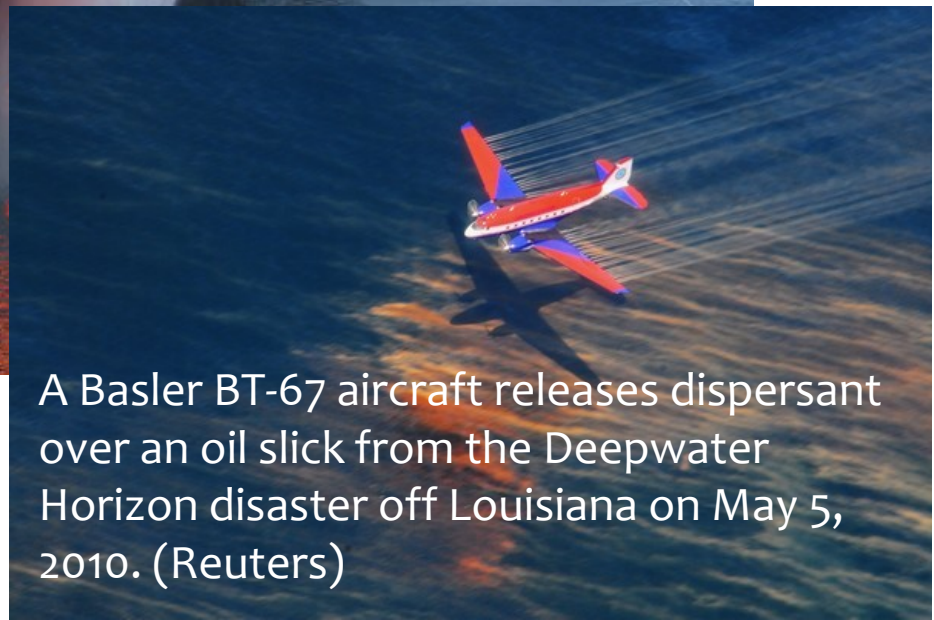
Summarizing results presented on two posters

Photo: US Coast Guard

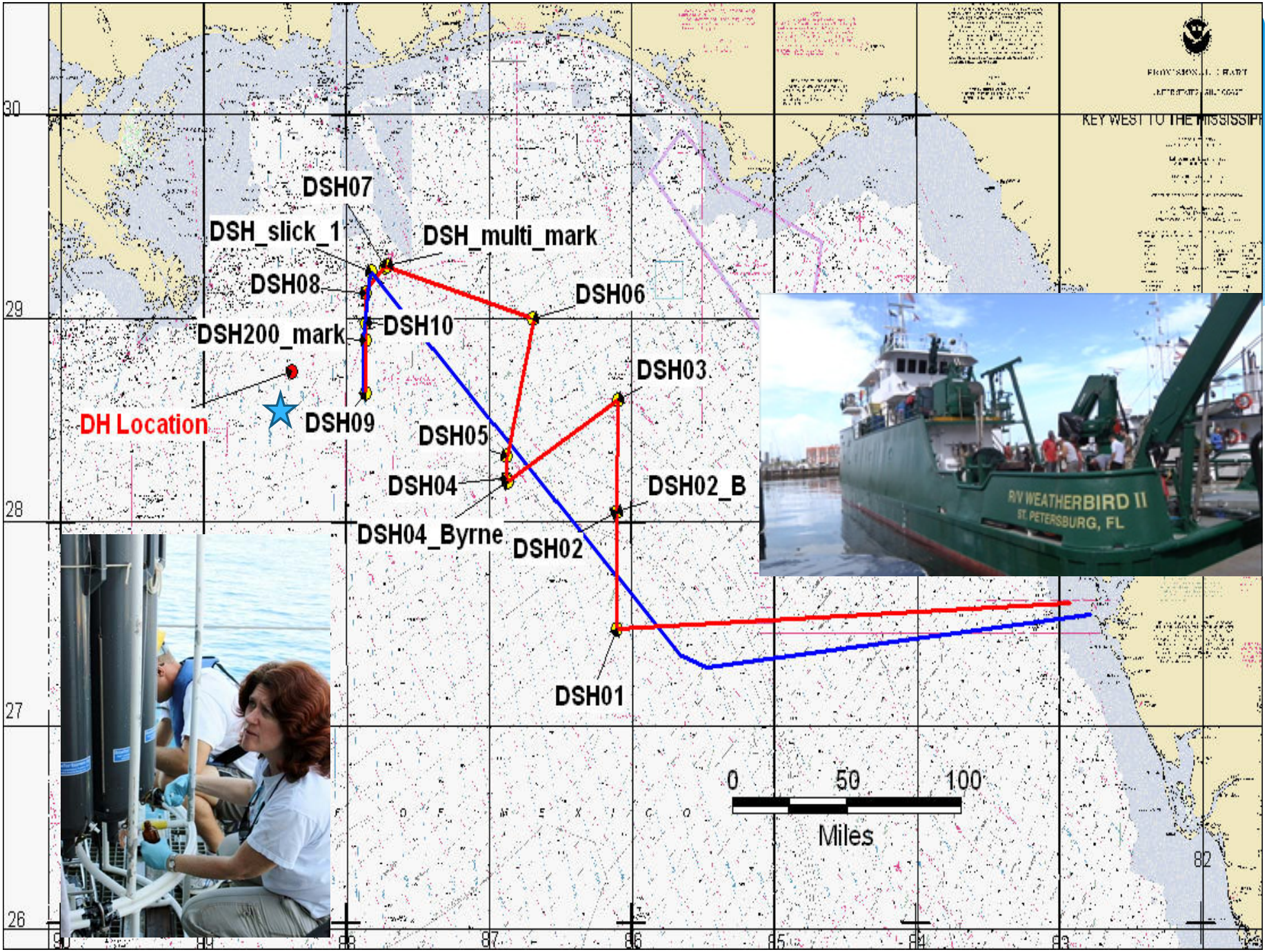
Deepwater Horizon Spill



Corexit 9500 applied via jet introduced into the petroleum hydrocarbons flowing from the wellhead.



A Basler BT-67 aircraft releases dispersant over an oil slick from the Deepwater Horizon disaster off Louisiana on May 5, 2010. (Reuters)


DSH07
DSH_slick_1
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DSH03
DH Location
DSH09
DSH05
DSH04
DSH02_B
DSH04_Byrne
DSH02
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0
50
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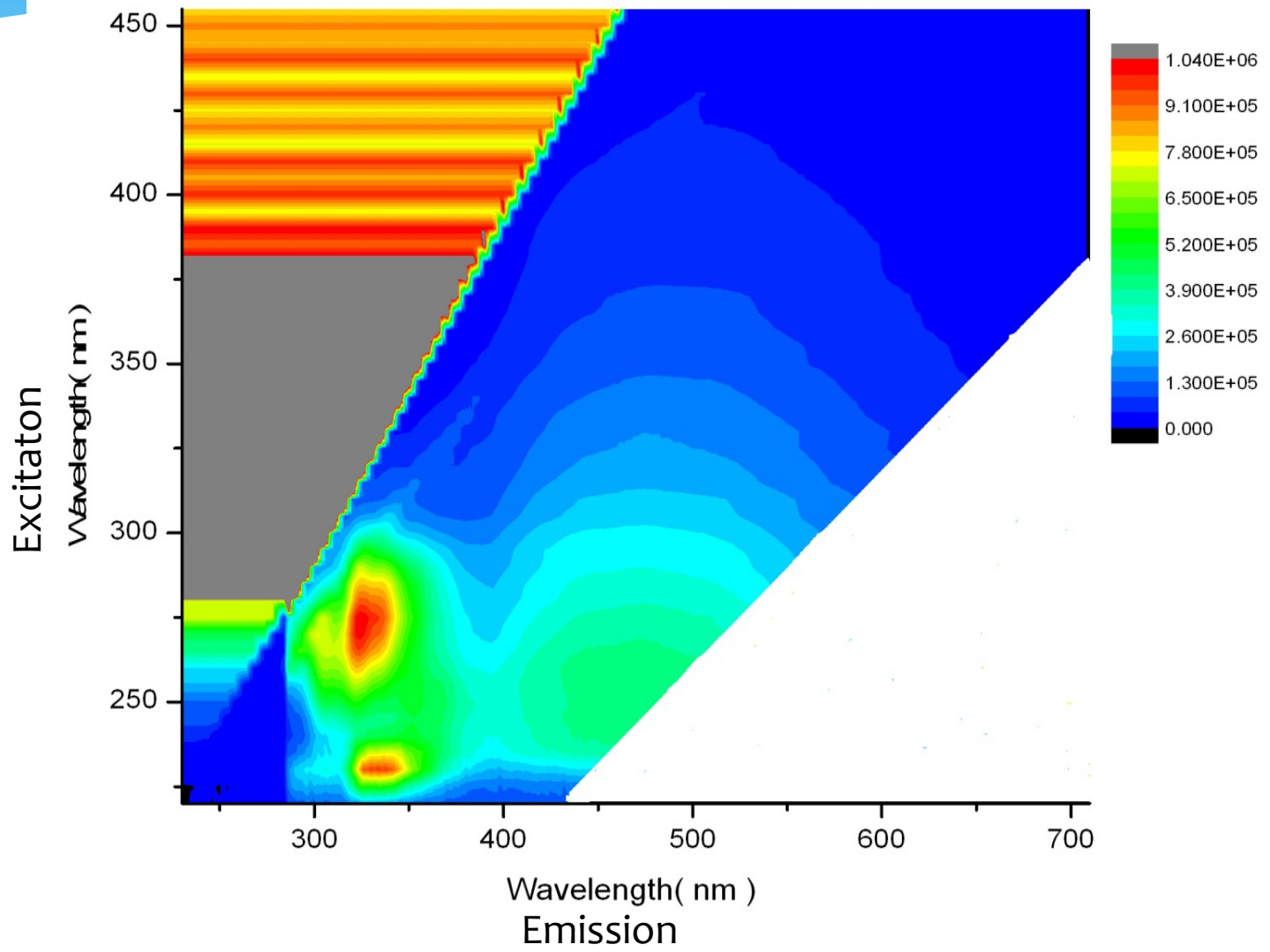
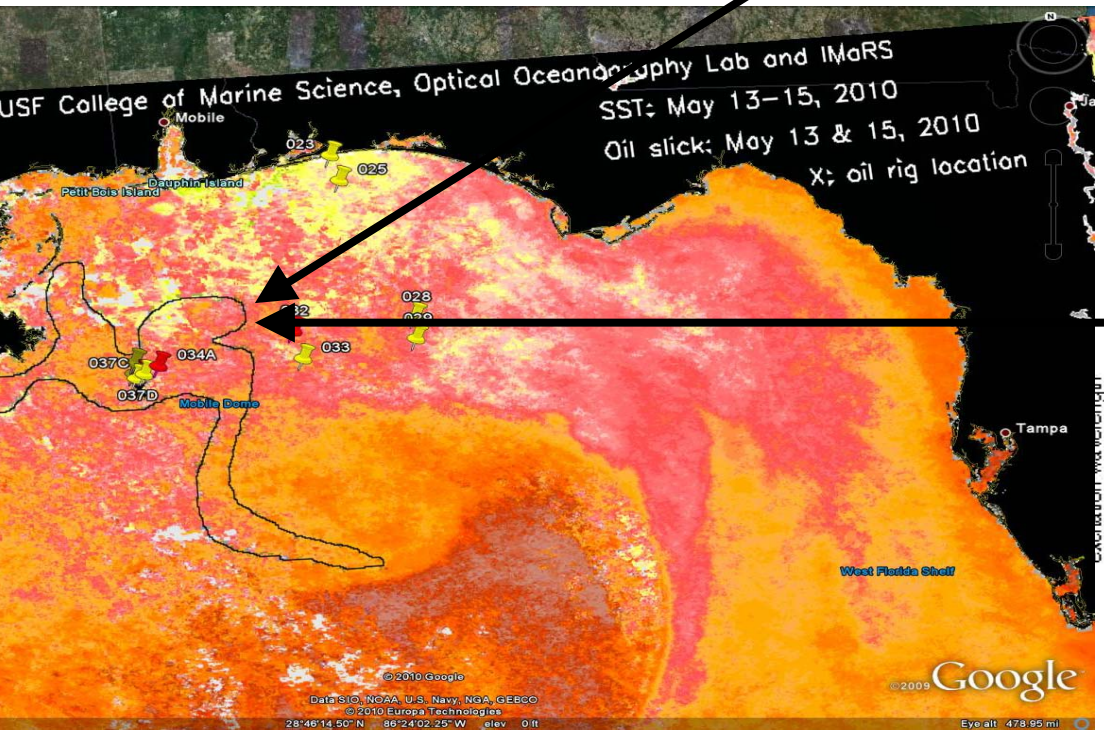
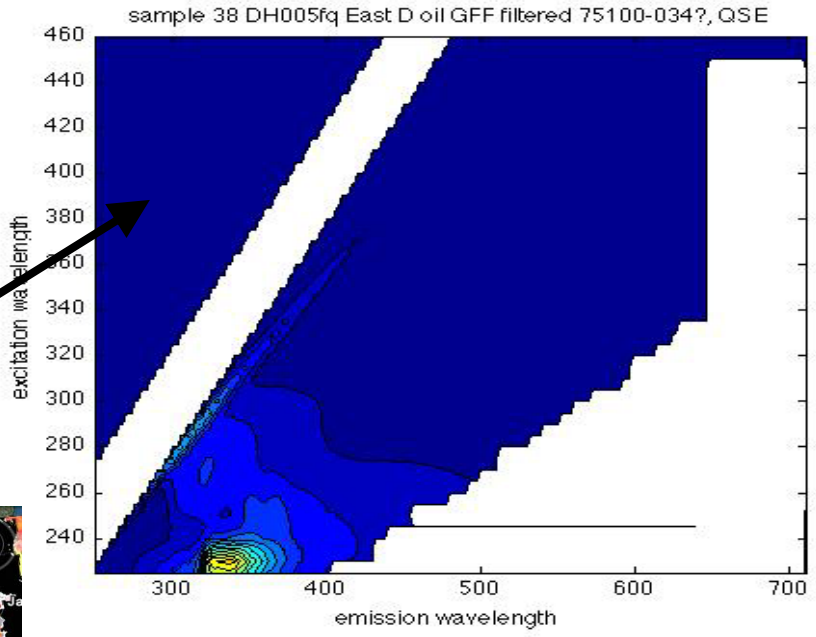
Miles
R/V WEATHERBIRD II
ST. PETERSBURG, FL
KEY WEST TO THE MISSISSIPPI

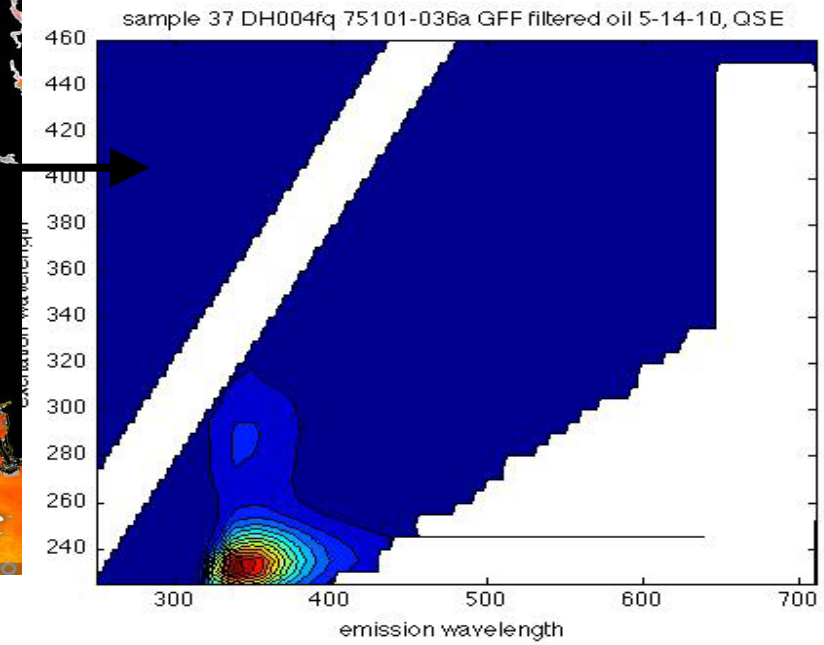
Dispersed MC252 Oil



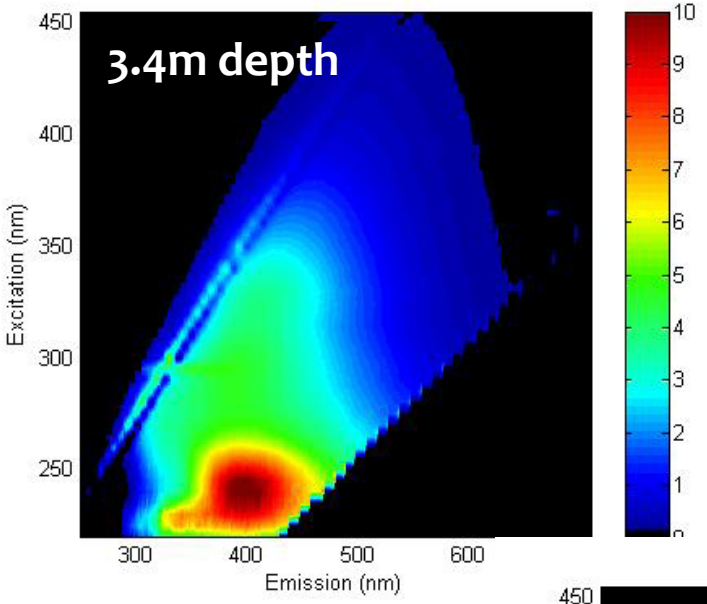
Surface Samples May 2010

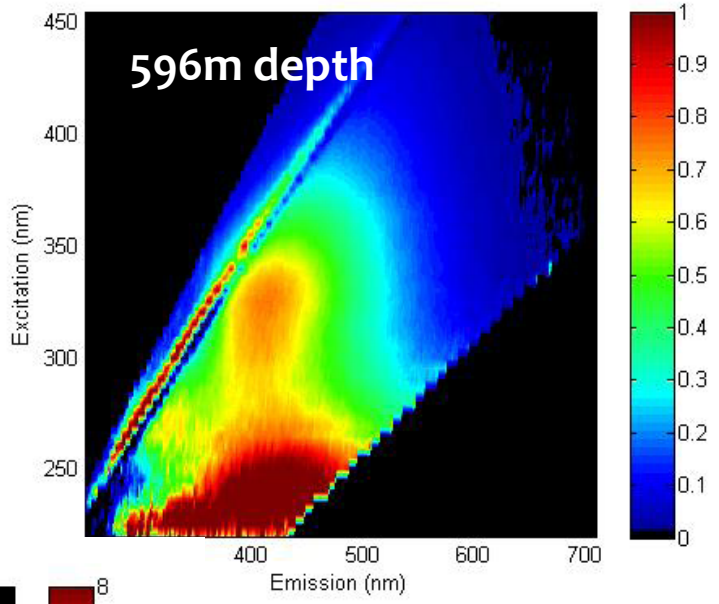


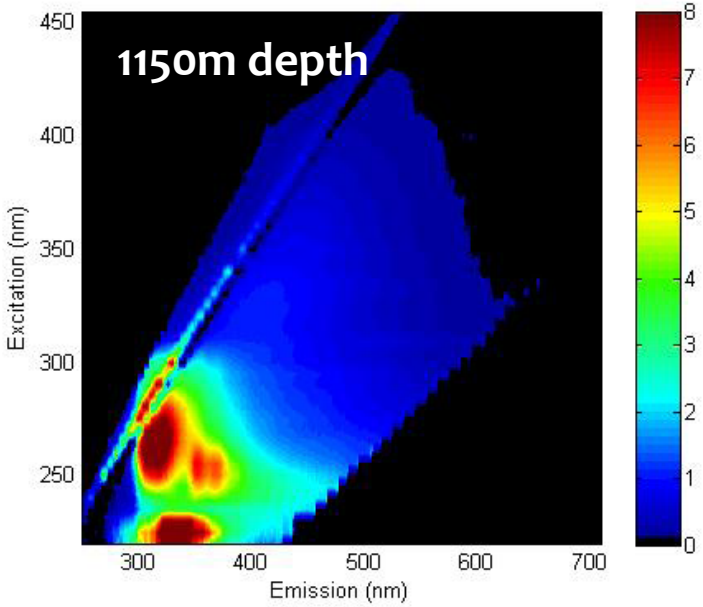




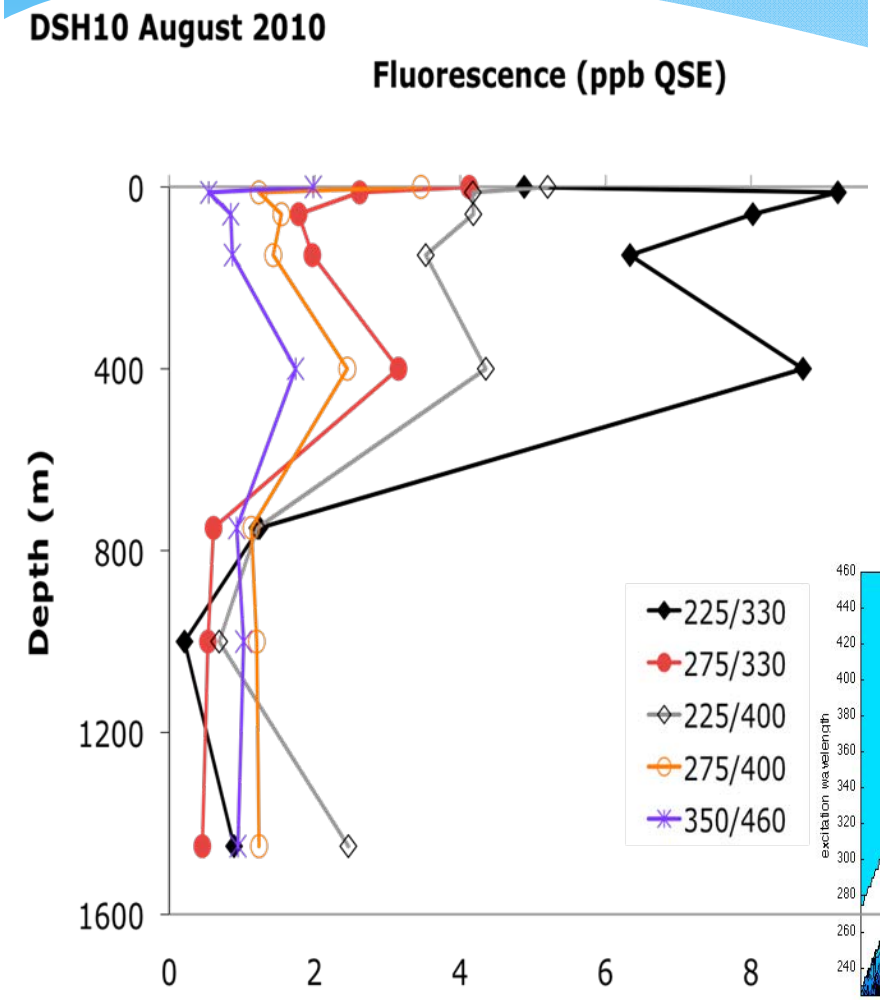
R/V Nancy Foster Cruise

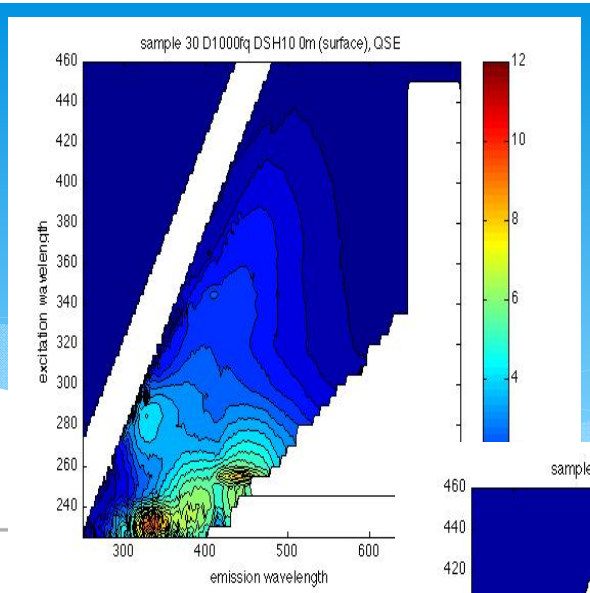


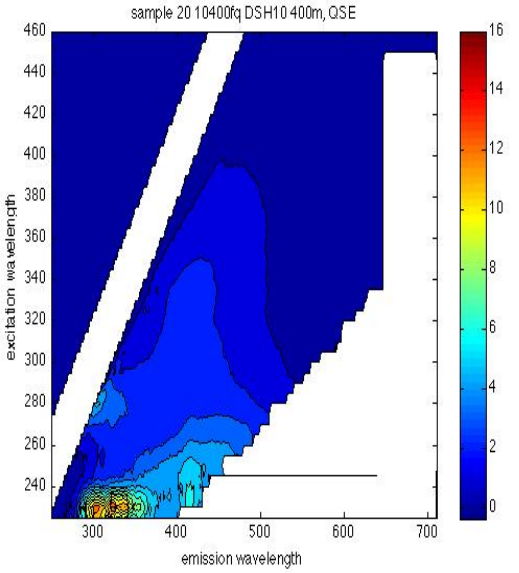


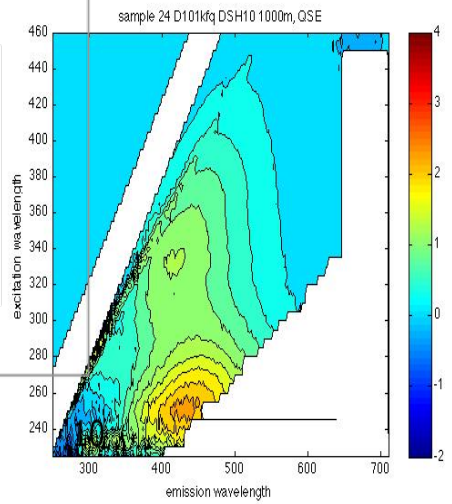


Oil in the Water Column

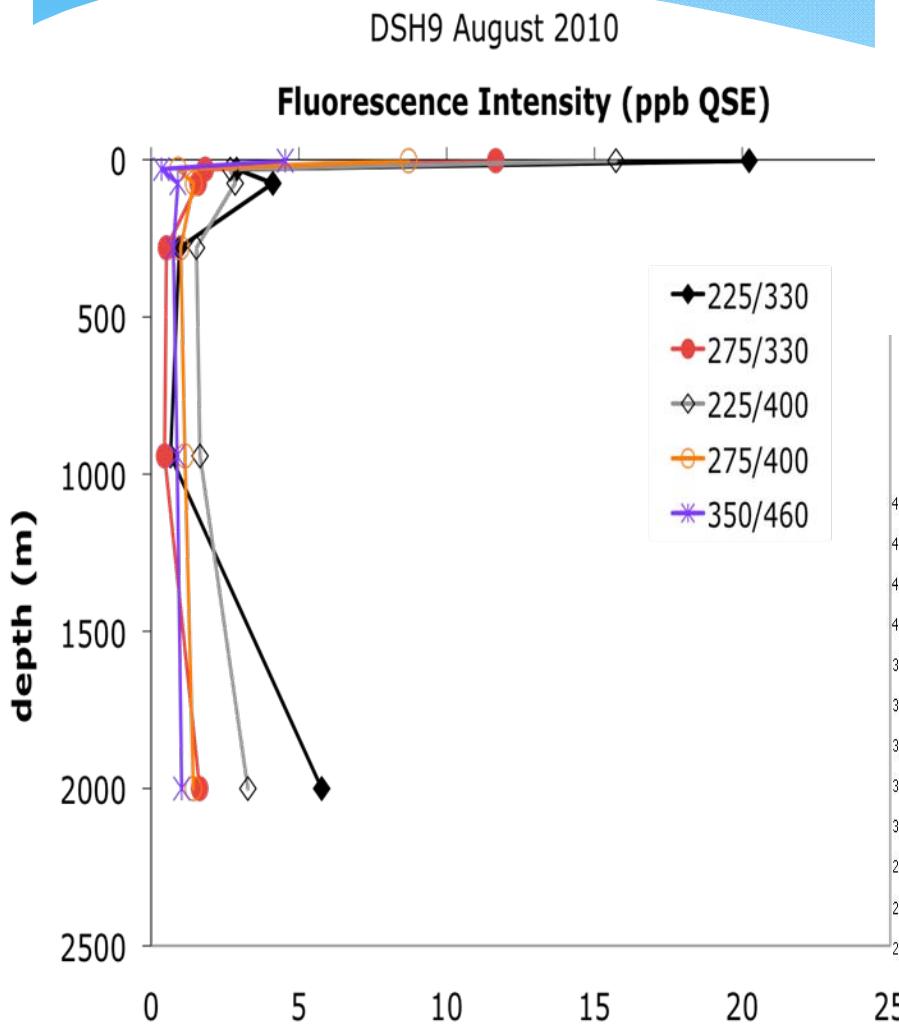


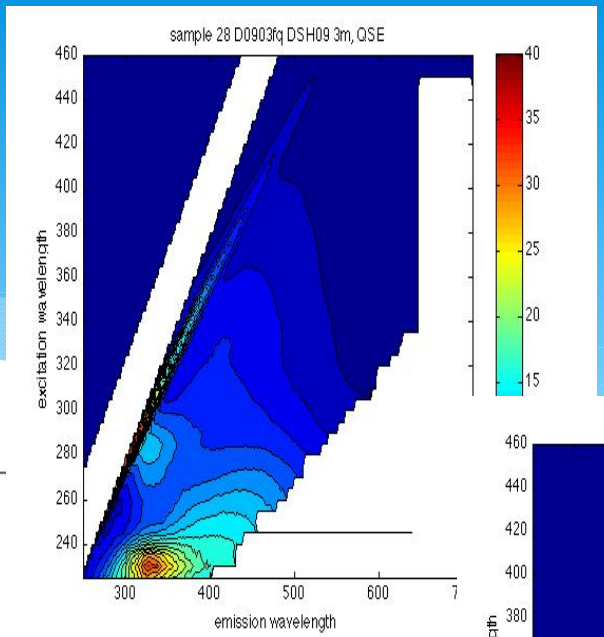


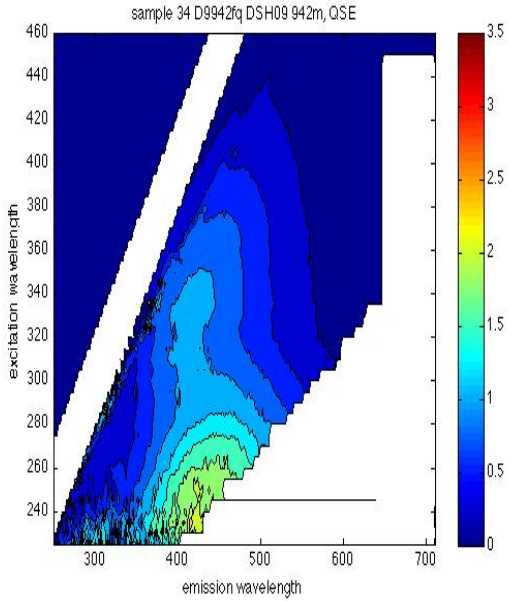


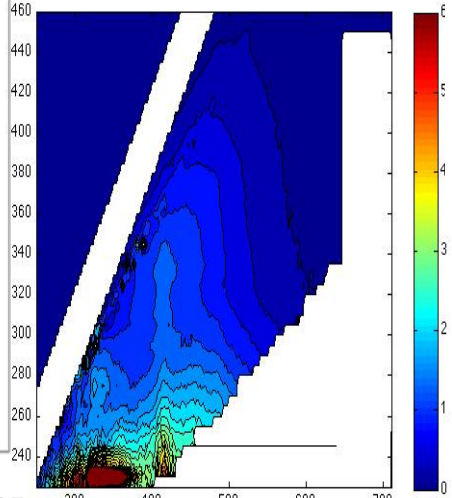


Oil in the Water Column









Continuing Research…

- Wave tank experiments at Bedford Institute of Oceanography, Department of Fisheries & Oceans, Nova Scotia, Canada
- Hydrocarbon sensor trials (ACT) with a wide range of instruments
- Further field and lab experiments, statistical analyses
- Analysis of archived field data, samples collected on additional cruises
  - December 2010, February and May 2011

BIO Workshop

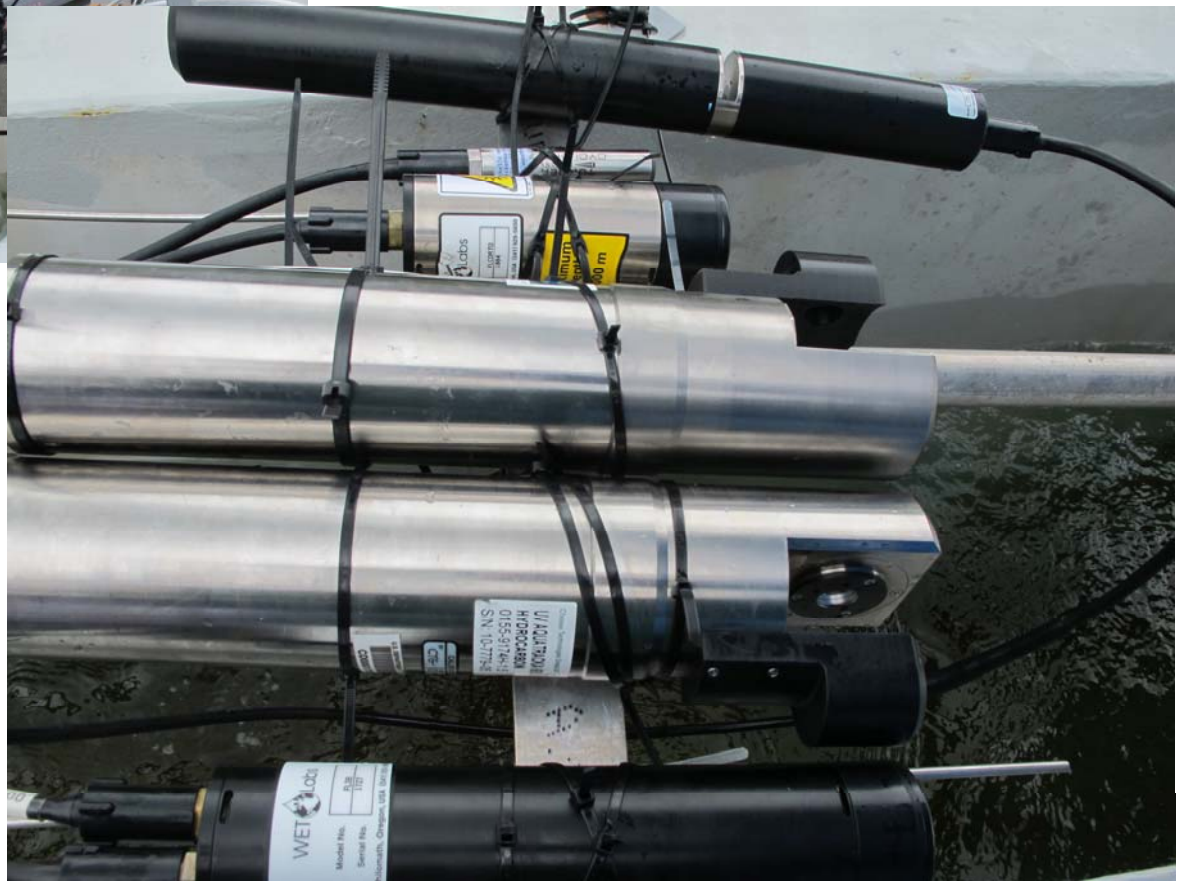
BIO Workshop

Protocol

- 15 separate wave tank experiments conducted; including 8 core experiments:
  - 100ml artificially weathered oil without dispersant
  - 100ml artificially weathered oil with dispersant (1:25 DOR)
  - 100ml fresh oil without dispersant
  - 100ml fresh oil with dispersant (1:25 DOR)
  - fluorescence properties of dispersant alone also examined
- Oil/dispersant in fixed volume of seawater
- Final concentration of 100ml oil/seawater in tank <7 ppm
- Core experiments run with the wave tank in flow-through mode
- Real-time *in situ* data collected with 7 different *in situ* instruments
- samples collected at t=0, 2,4, 6, 8, 10, 15, 20, 30, 45 60, 75, and 90 minutes for EEMS analysis Tank drained and cleaned between experiments

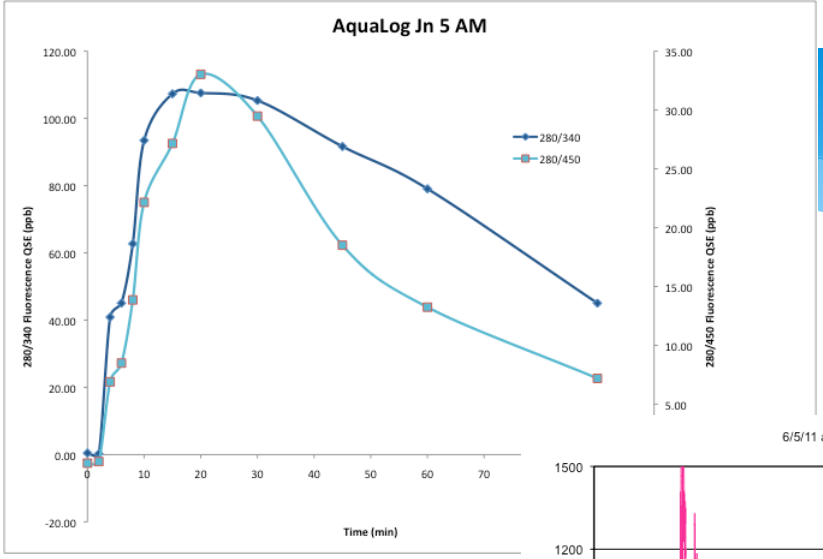
Instruments Tested

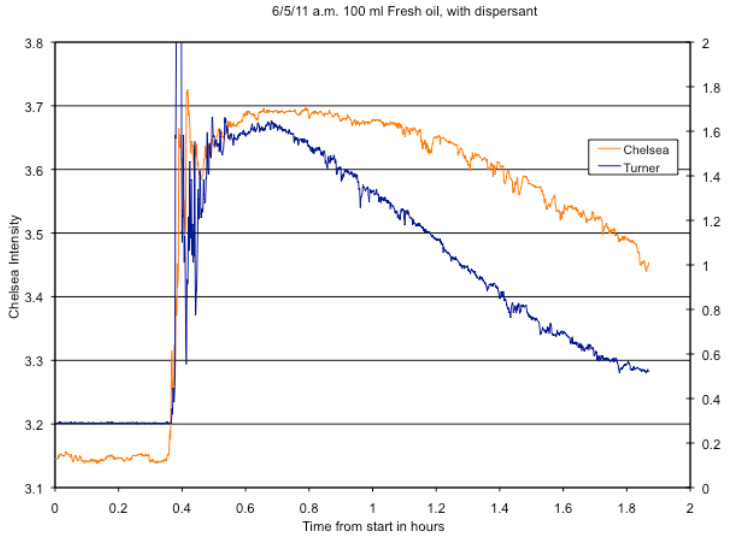
Instrument	Rationale for Inclusion in Experiment	Excitation	Emission
Chelsea UV-AQUAtracka for Crude Oil	widespread use in oil spill response August 2010 and beyond	239 ± 4 nm (26 ±4 nm FWHM)	360 ± 6 nm (70 ± 10 nm FWHM)
Chelsea UV-AQUAtracka for Refined Oil/CDOM	comparison with crude oil instrument	239 ± 4 nm (26 ±4 nm FWHM)	430 ±6 nm (110 ± 17 nm FWHM)
Turner Cyclops C-7 for Hydrocarbons	used by AOML and SWFSC on surveys, added to some SEAKEYS moorings	<300nm	300-400nm
WetLabs ECO-CDOM sensor	widespread use in oil spill response, especially May-August 2010	370nm	460nm (90 nm FWHM)
WetLabs ECO-Triplet for CDOM	used up EPA	370nm	420, 460, and 500nm (50nm FWHM)
WetLabs SAFire	prototype of next generation in situ oil/CDOM fluorometer	multiple	multiple
Satlantic SUNA UV Spectrophotometer	possible new type of sensor		
Horiba Aqualog	EEMS comparison	220-455nm (5nm increments)	250-700nm (5nm increments)
Shimadzu Spectrofluorometer	EEMS comparison		

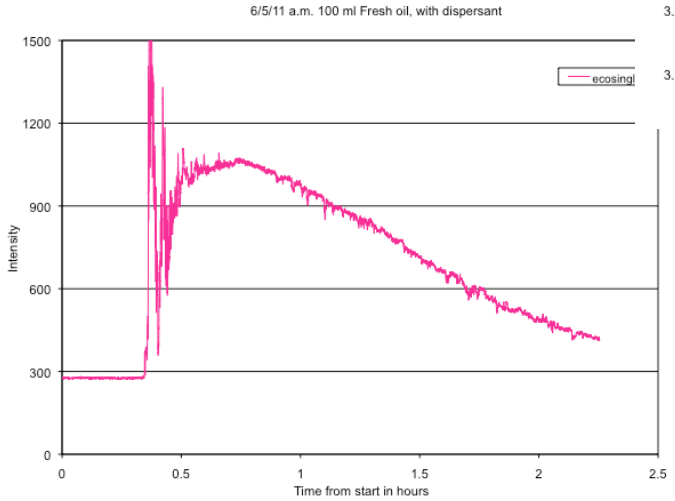

WET Labs

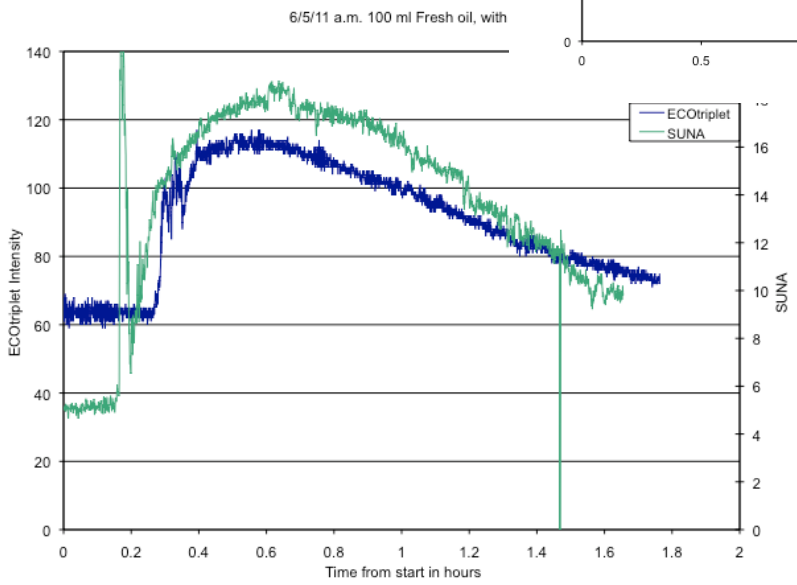
June 5 PM
100 ml fresh oil
no dispersant

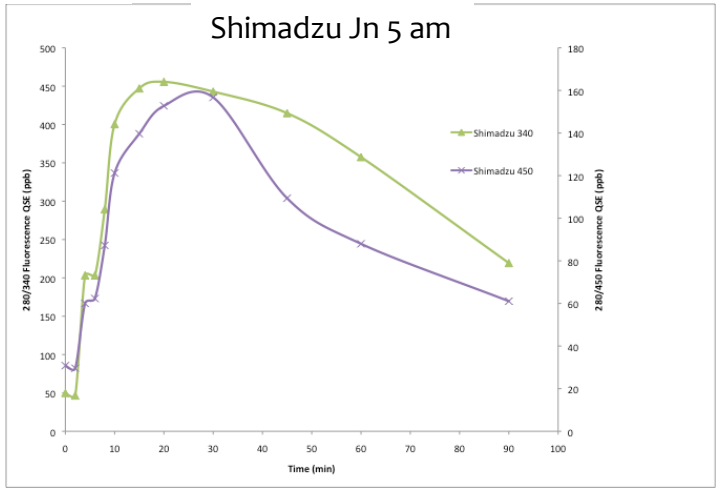
June 5 AM
100ml Fresh Oil with dispersant
DOR 1:25

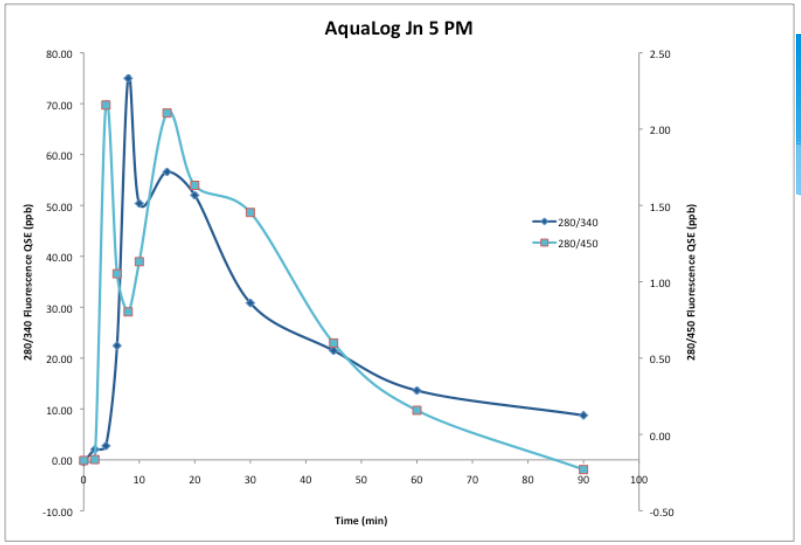

AquaLog Jn 5 AM
280/340
280/450
280/340 Fluorescence QSE (ppb)
280/450 Fluorescence QSE (ppb)
Time (min)

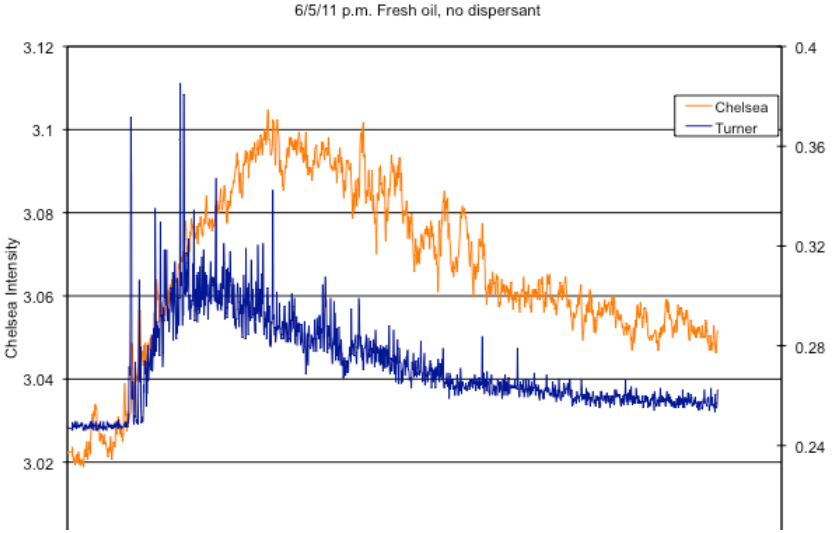

6/5/11 a.m. 100 ml Fresh oil, with dispersant
Chelsea
Turner
Chelsea Intensity
Time from start in hours

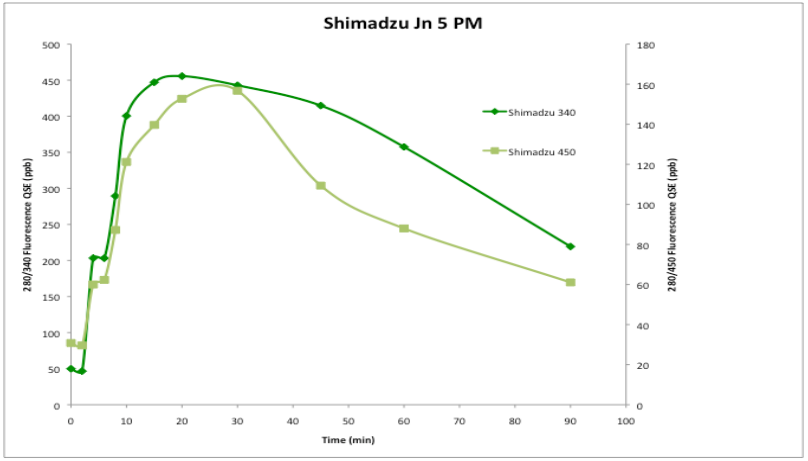

6/5/11 a.m. 100 ml Fresh oil, with dispersant
ecosingl
Intensity
Time from start in hours

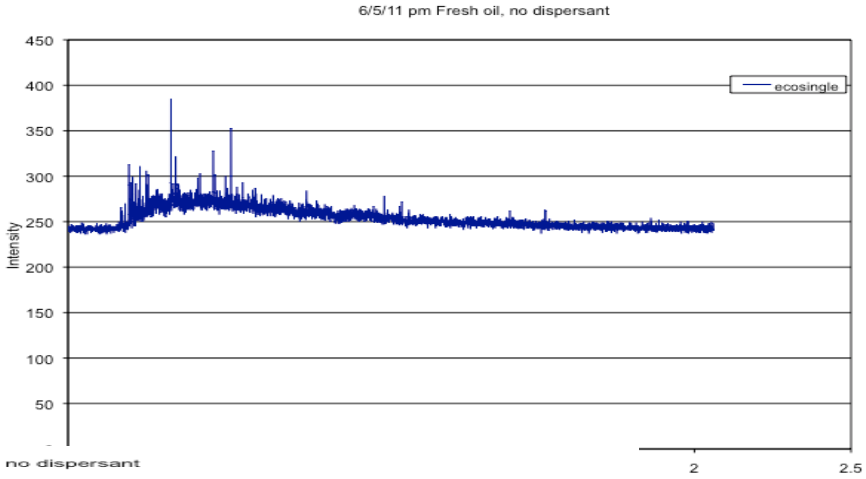

6/5/11 a.m. 100 ml Fresh oil, with
ECOtriplet
SUNA
ECOtriplet Intensity
SUNA
Time from start in hours

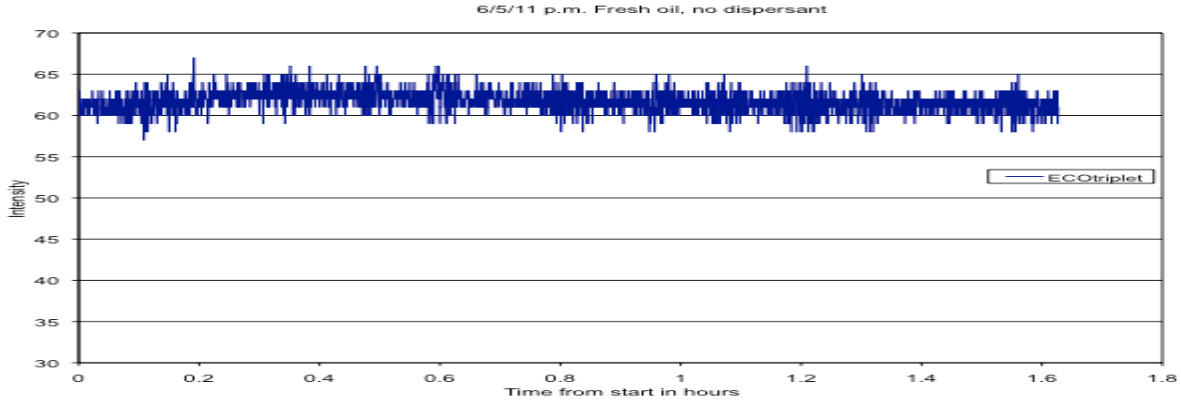

Shimadzu Jn 5 am
Shimadzu 340
Shimadzu 450
280/340 Fluorescence QSE (ppb)
280/450 Fluorescence QSE (ppb)
Time (min)

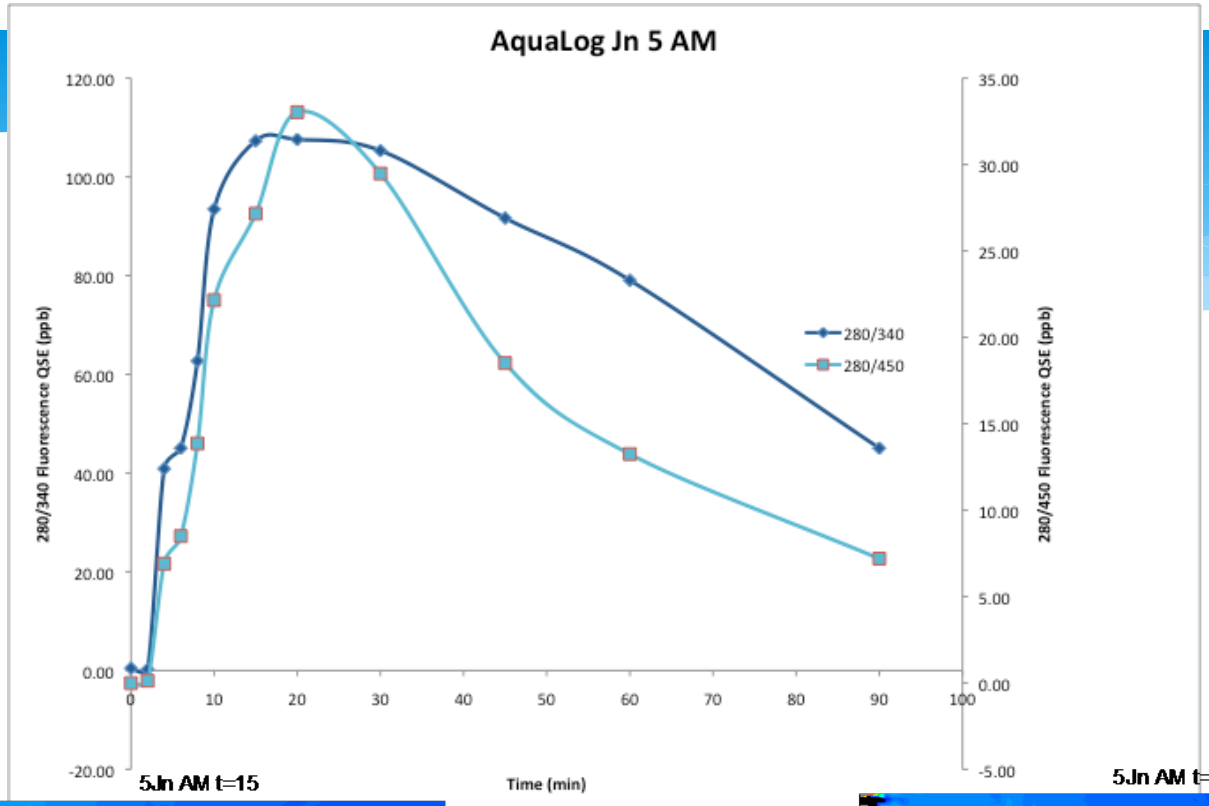

AquaLog Jn 5 PM
280/340 Fluorescence QSE (ppb)
280/450 Fluorescence QSE (ppb)
Time (min)
280/340
280/450


6/5/11 p.m. Fresh oil, no dispersant
Chelsea Intensity
Chelsea
Turner


Shimadzu Jn 5 PM
280/340 Fluorescence QSE (ppb)
280/450 Fluorescence QSE (ppb)
Time (min)
Shimadzu 340
Shimadzu 450


6/5/11 pm Fresh oil, no dispersant
Intensity
ecosingle


6/5/11 p.m. Fresh oil, no dispersant
Intensity
ECOtriplet
Time from start in hours


AquaLog Jn 5 AM
280/340 Fluorescence QSE (ppb)
280/450 Fluorescence QSE (ppb)
Time (min)
280/340
280/450
120.00
100.00
80.00
60.00
40.00
20.00
0.00
-20.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
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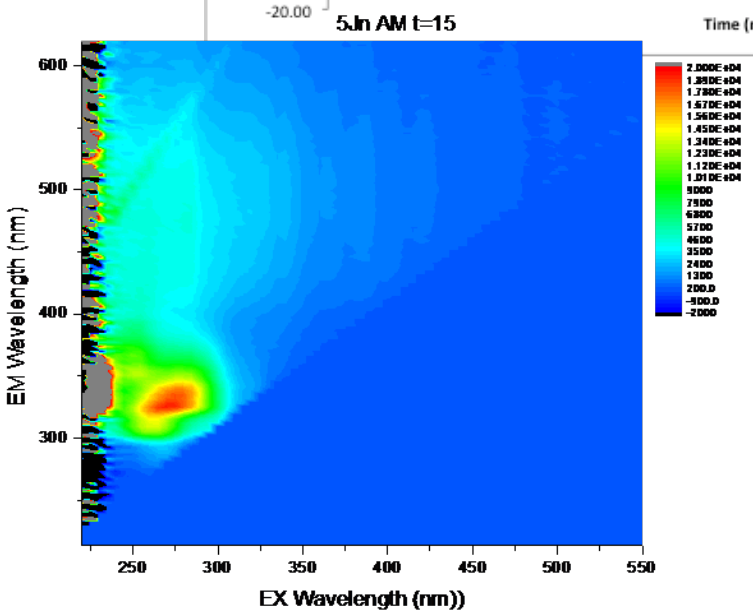
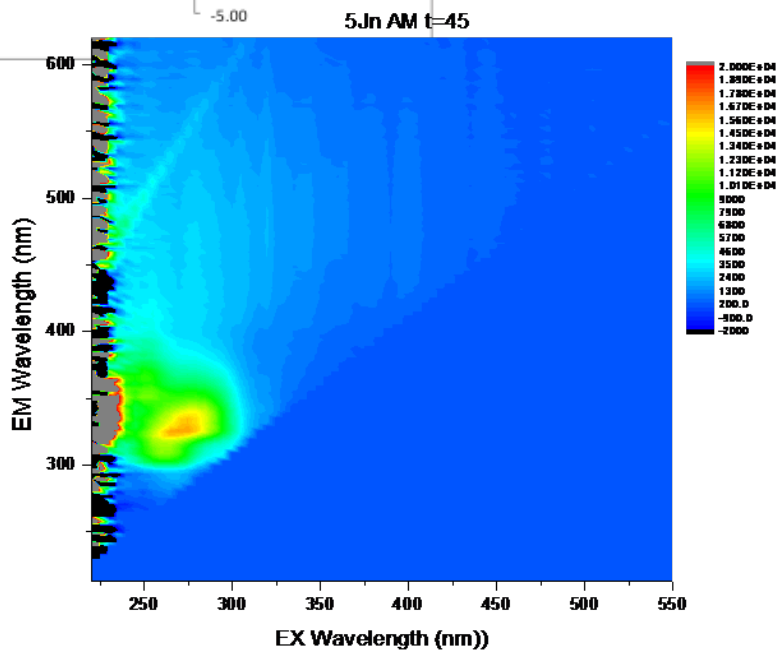
0
10
20
30
40
50
60
70
80
90
100


5Jn AM t=15
EM Wavelength (nm)
EX Wavelength (nm))
600
500
400
300
250
300
350
400
450
500
550


5Jn AM t=45
EM Wavelength (nm)
EX Wavelength (nm))
600
500
400
300
250
300
350
400
450
500
550

Conclusions

- All instruments were responsive to changes in oil concentration, slightly different responses due to different wavelengths
- EEMS from water samples collected near the Deepwater Horizon site in May and August 2010 were similar to those from the tank experiments at $t \geq 45$ minutes.
- Intensity and spectral properties of the fluorescence fingerprint are affected by oil concentration and dispersant to oil ratio (DOR).
- Presence of dispersant may have influenced EEMs collected from the Deepwater Horizon spill site.

Thanks to:

Fisheries and Oceans Canada

Pêches et Océans Canada

Captain Matt White & the crew of the R/V Weatherbird II, the staff at COOGER, Lore Ayoub and Ana Arellano

Please come to the poster session

Fluorescence-Based Detection of Oil and Oil-Dispersant Mixtures in Seawater

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Tracking Oil Dispersion in the Gulf of Mexico by Fluorescence Spectroscopy

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