# Submersible optical sensors exposed to chemically-dispersed crude oil: wave tank simulations for improved oil spill monitoring

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## Background

The SMART (Special Monitoring of Applied Response Technologies) guidance protocols call for the use of fluorescence techniques to assist in decision-making for burning or dispersant operations during oil spills (SMART report, 2006). Recommendations on fluorometer optical configuration, capability, and application in subsea environments however, are not currently considered in this document. During the Deepwater Horizon Spill of National Significance various submersible fluorometers were deployed, providing critical *in situ* measurements for tracking the subsea plume of dispersed oil. In the wake of the spill many questions remained as to sensor dynamic range, minimum detection limits, and optimum wavelength configuration (JAG report, 2010). Confounding proper sensor selection are the effects of oil concentration, dispersant to oil ratio (DOR), oil type and dispersant type on dispersant effectiveness (Lee et al., 2009) and fluorescence signatures (Kepkay et al., 2008). All of which lead to uncertainties in selecting sensors best-equipped to detect or quantify dispersed oil in the field. Sensor reliability in detecting dispersed oil in the field is additionally problematic when calibrations are conducted within laboratory flasks, at elevated standard concentrations, and with insufficient mixing energies (Fuller et al, report; JAG report, 2010). To address these uncertainties the performance of commercially-available fluorometers and a spectrophotometer, some of which were deployed during the DWH spill, was evaluated using the Bedford Institute of Oceanography wave tank facility.

## Experimental Design

Experiments of sensor performance were conducted using weathered and fresh MC252 crude oil and Corexit 9500 dispersant at a DOR of 1:25 in a wave tank, capable of reproducibly generating waves (Figure 1). Breaking waves were generated to simulate mixing energies and achieve dispersant effectiveness observed in the field. Water from Halifax Harbor was pumped into the wave tank through a coarse (25 um pore size) and fine (5 um pore size) filtration system prior to experiments, and emptied and cleaned afterwards to remove all oil and surfactants.

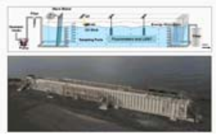
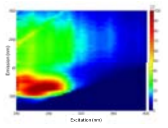


*Figure 1. BIO wave tank in Dartmouth, Nova Scotia measures 32m L x 0.6m W x 2m D).*

Submersible fluorometers, a spectrophotometer, and a particle size analyzer (Figure 2) were mounted onto a metal rack and deployed within the tank located 20 m from the wave generator. Discrete samples were collected at various time points throughout the experiments and analyzed for Total Petroleum Hydrocarbons (TPH), Benzene-Toluene-Ethylbenzene-Xylene (BTEX) & Polycyclic Hydrocarbons (PAH).



○ **FI Ratio** = $F_{280/340\,:\,280/445}$

☐ **Chelsea Technologies**
AQUAtracka oil $F_{239/360}$
AQUAtracka gelbstoff $F_{239/440}$

△ **Turner Designs**
Cyclops crude oil $F_{320/510}$

◇ **WET Labs Inc.**
ECO single $F_{370/460}$
Triplet $F_{370/420,465,500}$
SAFIre $F_{96\ \lambda\ pairs}$

**Satlantic**
SUNA $_{ABS190\text{-}370}$

**Sequoia**
LISST 100X

*Figure 2. Fluorescence EEM of 12 ppm MC252 crude oil, DOR 1:25. Symbols represent approximate CWLs of fluorometers used in the study. The Fluorescence Intensity Ratio (FIR) for oil discrimination is shown for reference.*

## Stepwise Experiment

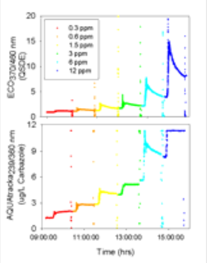


*Figure 3. Fluorescence output for select sensors during the oil addition experiment.*

- •Additions of fresh oil (300 ppb – 12 ppm, DOR=1:25) to tank operated in static-mode.
- •Oil and dispersant added each hour to allow tank to homogenize prior to adding subsequent concentrations.
- •Manufacturer calibrations applied to data streams.
- •Final 5 minutes of sensor data for each concentration was averaged and then regressed to [BTEX ] & [TPH].
- • Used to establish linearity of sensors to MC252 oil.

•All sensors detected oil down to 300 ppb, countering the perception during the DWH Spill that 1 ppm may be the LDL of some models. AQUAtracka sensors saturated at 12 ppm oil.

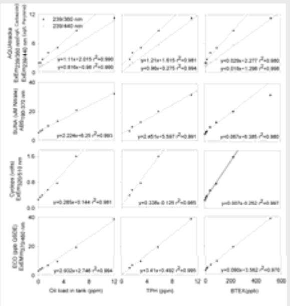


*Figure 4. Regression equations for estimating [oil] (TPH and BTEX ) from in situ sensors.*

## Core Experiments

- •10 core tank experiments of fresh and weathered oil, with and w/o dispersant at oil (3 ppb , DOR=1:25).
- •Tank operated in continuous flow mode to simulate peak and dilution of oil plume.
- •Stepwise regressions used to calibrate data and estimate [BTEX ] & [TPH].
- •Sensor performance and calibration validated with chemistry results in each run.

Examined Sensor Performance as a function of:

1. Presence of dispersant
2. Oil state (Fresh and Weathered dispersed oil)
3. Degree of Dispersant Effectiveness
4. Dilution of oil plume

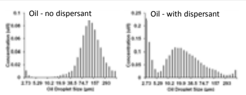


*Figure 5. Particle size analysis for experiments with and w/o dispersant. Corexit increases fluorescent signal by removing oil droplets from air-water interface and suspending them within the water. Only dispersed oil results are shown below.*

•Estimated [oil ] (sensor) well correlated to measured [oil] (discrete samples) for both **FRESH** and **WEATHERED** oil.

•Presence of dispersant reduced oil droplet size and increased fluorescence signal throughout water column in tank.

•Variations in plume dilution did not influence sensor performance in estimating oil concentration.

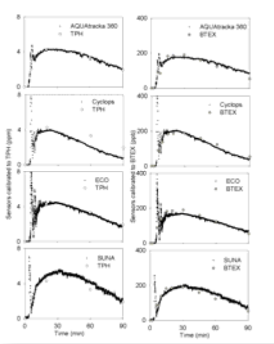


*Figure 6. Estimated (sensors) and measured oil (TPH & BTEX ) concentrations during simulated oil plume dilution with **GRADUAL** decay.*

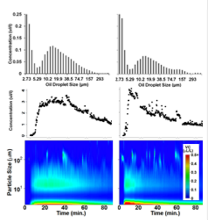


*Figure 7. Particle size distribution and concentration within wave tank. Histograms are composites of entire flow-through experiment. Total particle concentration as a function of time (middle) is shown in scatter plot. Contour plots represent Particle size and volume concentration as a function of time for chemically-dispersed MC252 crude oil with gradual (left) and rapid (right) decay.*

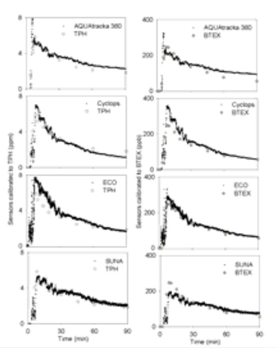


*Figure 8. Estimated (sensors) and measured oil (TPH & BTEX) concentrations during simulated oil plume dilution with **RAPID** decay.*

## Sensor Performance Findings

Results in Conmy et al., (accepted) Environmental Science & Technology

*Table 1. Percent differences (%$_{dif}$) between sensors and chemistry. Asterisk represents sensor with only one experiment. MAE is Mean Absolute Error.*

| | | TPH (ppm) | | | | | BTEX (ppb) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | ECO 370/460nm | AQUA 239/360nm | AQUA 239/440nm* | Cyclops 320/510nm | SUNA ABS | ECO 370/460nm | AQUA 239/360nm | AQUA 239/440nm* | Cyclops 320/510nm | SUNA ABS |
| All time points | mean %$_{dif}$ | 31.69 | 30.24 | 41.98 | 40.32 | 27.92 | 26.67 | 30.93 | 23.14 | 31.99 | 30.45 |
| | median %$_{dif}$ | 23.54 | 21.15 | 26.21 | 25.54 | 15.68 | 13.66 | 20.95 | 12.34 | 24.41 | 23.74 |
| | min %$_{dif}$ | 0.27 | 1.96 | 2.16 | 1.73 | 0.76 | 1.63 | 3.19 | 5.29 | 0.01 | 0.65 |
| | max %$_{dif}$ | 183.78 | 186.85 | 194.19 | 199.92 | 214.04 | 122.22 | 128.82 | 85.95 | 114.40 | 140.97 |
| | [MAE] | +/- 0.91 | +/- 0.67 | +/- 0.78 | +/- 0.90 | +/- 0.68 | +/- 23.53 | +/- 13.46 | +/- 12.41 | +/- 32.22 | +/- 27.68 |
| Time points > 10 min | mean %$_{dif}$ | 25.52 | 19.37 | 19.22 | 30.94 | 13.88 | 15.54 | 23.88 | 14.17 | 21.11 | 22.85 |
| | median %$_{dif}$ | 23.85 | 18.72 | 23.87 | 21.29 | 11.20 | 12.00 | 15.14 | 7.96 | 16.67 | 19.95 |
| | min %$_{dif}$ | 0.27 | 1.96 | 2.16 | 1.73 | 0.76 | 1.63 | 3.19 | 5.29 | 0.01 | 0.65 |
| | max %$_{dif}$ | 74.55 | 53.83 | 35.22 | 127.31 | 46.00 | 85.57 | 83.18 | 31.26 | 87.71 | 81.00 |
| | [MAE] | +/- 0.78 | +/- 0.58 | +/- 0.81 | +/- 0.77 | +/- 0.47 | +/- 17.27 | +/- 12.43 | +/- 12.41 | +/- 29.13 | +/- 24.50 |
| % of > 10 min Time Points | < 25%$_{dif}$ | 56% | 72% | 57% | 56% | 90% | 86% | 68% | 86% | 64% | 63% |
| | < 30%$_{dif}$ | 69% | 84% | 71% | 60% | 97% | 91% | 71% | 86% | 79% | 74% |

### TPH

•SUNA better estimated TPH with 97% of time points within 30%$_{dif}$ and the lowest Mean Absolute Error.

### BTEX

•ECO and AQUAtracka $_{239/440}$ better estimated BTEX with 91% and 86% of time points within 30%$_{dif}$ and the lowest Mean Absolute Error.

## Subsea Injection Experiments (on going)

•Conduct tank experiments using ANS crude and IFO-120 oil with Corexit.
-DOR=1:25, 1:100, 1:250, 0
-Current velocity 1 – 5 cm/s
-Water temperature <8 and > 15°C

•Characterize dispersant effectiveness, droplet size distribution and numerical modeling to assess subsurface dispersant injection response options.

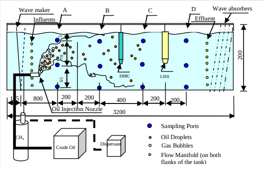


*Figure 9. Schematic representation (in cm, not to scale) of flow-through wave tank with subsea injection system.*

*Figure 10. Time lapse photos of subsurface injection of oil with and without dispersant.*

## Next Steps & Implications

•Apply regressions to DWH Spill sensor data to estimate oil concentration in subsea plume.

•Evaluate EEM and chemistry results to determine changes in optical signatures during dilution of oil plumes.

•Findings will inform recommendations on technological needs. This is timely, as proposed amendments to the National Oil and Hazardous Substances Pollution Contingency Plan (NCP) are now calling for sensor specifications and capabilities to be specified.

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## Citations & Acknowledgements

Fuller et al. Field Instruments for Real Time In-Situ Crude Oil Concentration Measurements. Texas A&M University report, 10 pp.

Joint Analysis Group Report (2010) Review of data to examine subsurface oil in the vicinity of DWH MC-252, May 19-June 19, 2010, 29 pp.

Kepkay, et al. (2008) UVfluorescence spectroscopy (UVFS): A new means of determining the effectiveness of chemical dispersants on oil spills. International Oil Spill Conference. API, Washington D.C., Savannah, GA, pp. 639-44.

Lee et al. (2009) Wave tank studies on dispersant effectiveness as a function of energy dissipation rate and particle size distribution. Report to NOAA/CRRC/UNH, 67 pp.

Special Monitoring of Applied Response Technologies (2006) Protocol report developed by US CG, NOAA, US EPA, CDC, MMS, 43 pp.