Robust tools to detect subsurface oil: fluorescence sensors

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Abstract: New instruments to detect sub-surface oil in natural waters have been developed by Sea-Bird Scientific. The new instruments build upon the lessons of the Deepwater Horizon response and subsequent scientific research. Improvements in optics, electronics and instrument design have enabled a factor of five increased sensitivity in fluorescent dissolved organic matter (FDOM) sensors which respond to crude oil. Signal confirmation of the presence of oil from FDOM sensors has been enhanced with single housing multiple sensor instruments. Further reduction of false positives relies on the use of newly available UV-C LEDs to measure changes in fluorescence signals as fractional components of crude oil dissolve out of droplets.

Keywords: oil detection, fluorescence, backscattering

I. Introduction:

A variety of sensors and associated methodologies are available to detect sub-surface oil. However, the field of robust tools is much smaller. Sea-Bird Scientific is developing technologies for a family of oil detection sensors that are both more effective and more robust than current sensors.

For sub-surface oil detection, we define robustness as encompassing both research and industrial applications. Specifically, robustness is defined as methods that:

- Do not require significant expertise to deploy
- Work within standard deployment frameworks
- Do not require extensive pre- or post-deployment tests
- Have low rates of false positives
- Have low rates of false negatives

Single wavelength excitation ultraviolet fluorometers were effective in detecting the deep plume associated with the Deep Water Horizon. In that event, the source was known and large and the near field subsea environment was well characterized such that anomalies in the fluorescence signal could be easily associated with the source. Particularly in the deepest oil plume (1100 to 1300 m) fluorescence anomalies were associated with positive beam attenuation anomalies (Diercks et al., 2010). Where sources and environments are less well defined, having multiple corroborative data sources will increase confidence in oil detection.

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For more general work, such as detecting leaks from existing structures, tracking smaller plumes, and distinguishing natural seeps from anthropogenic sources, positively discriminating oil from other fluorescing substances is more challenging. This is especially true in highly variable environments such as shallow waters and where significant fresh water sources exist.

Single wavelength fluorometers have advantages but do not achieve robustness as defined above. Fluorometers have been used extensively in research and environmental studies and hence do not require significant special training to deploy and gather quality data. With relatively simple analog or serial output and generally low power requirements, single channel fluorometers are readily adaptable to standard data collection methods, e.g. profiling and underway flow through systems, as well as autonomous gliders and AUVs. Further, sensors with internal memory and batteries can be mechanically integrated onto vehicles of opportunity such as ROVs. Current instruments have relatively low limits of detections, with the most common fluorometers used in the Deep Water Horizon response able to detect oil in water at concentrations well below 1 ppm. Current sensors based on LEDs and silicon detectors have also been proven to be stable such that relatively simple pre and post deployment checks can establish data integrity.

To enhance the ability to detect oil in water Sea-Bird Scientific has developed a family of oil detection instruments which incorporate multiple optical channels (SeaOWL UV-A) and multiple fluorescence channels (SeaOWL UV-C and Crude Oil WET Star). Initial testing of the instruments has taken place at the Bedford Institute of Oceanography's COOGER facility flume.

II. SEAOWL UV-A:

The SeaOWL UV-A instrument incorporates a chlorophyll fluorometer for estimation of total plant material concentration, a 700 nm backscattering sensor for estimation of total particulate concentration and an FDOM fluorometer calibrated to quinine sulfate dehydrate for FDOM and an oil proxy for oil concentration. The backscattering and chlorophyll sensors in the SeaOWL help to discriminate increasing FDOM signals from phytoplankton blooms and sediment resuspension events.

Improvements in the SeaOWL UV-A's FDOM/oil channel have demonstrated a fivefold increase in resolution as compared to the ECO CDOM fluorometer, though they have the same excitation/emission parameters (370 nm EX, 460 nm EM).

Improvement in resolution for a particular sensor yields a decrease in the limit of detection. For oil in water sensors this effectively increases the ability to distinguish a leak from variability.

The SeaOWL UV-A, SeaOWL UV-C and the Crude Oil WET Star were tested at the Bedford Institute of Oceanography's COOGER facility with a series of oil injection experiments. These tests were piggybacked on a series of experiments with the instruments used during the Deep-Water Horizon response. The new sensors were displaced a few meters 'downstream' in the flume so that there was a temporal displacement of passage of the plume. Flow dynamics mixed the plume during the passage such that peak concentrations decreased as the volume of the plume increased. To demonstrate the coherence between the two instruments we plotted the plume with variable temporal and concentration scales to capture the structure of the plume as recorded by each instrument.

A. Increased Resolution

We estimate the relative increase in resolution between the ECO CDOM fluorometer calibrated for oil and the SeaOWL UV-A by comparing the calibrations of the instruments using quinine sulphate dehydrate.

Resolution for the ECO CDOM:	0.0306 QSDE/ count
Resolution for the SeaOWL UV-A:	0.0065 QSDE/ count

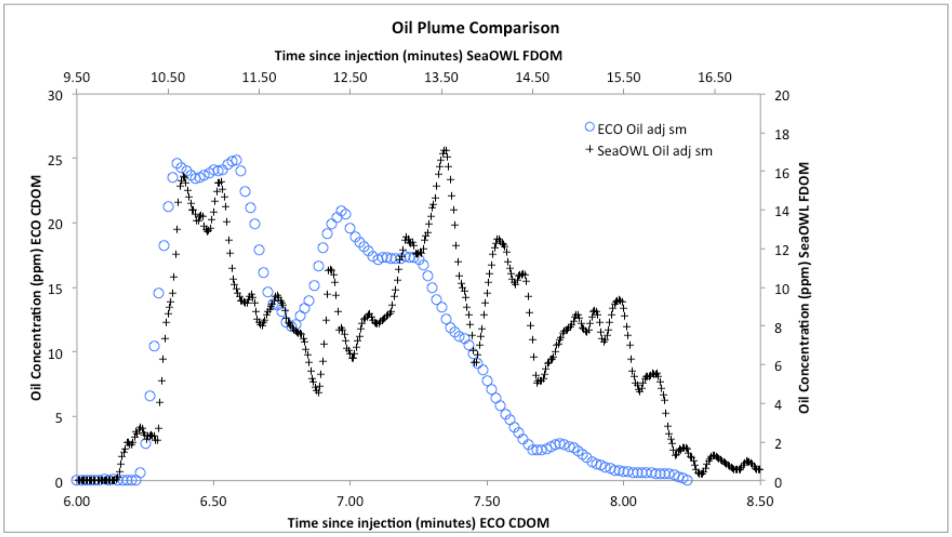
Applying the ECO CDOM crude oil calibration from Conmy et al., 2014 yields a scale factor in terms of oil concentration:

Resolution for the ECO CDOM:	10 ppb crude oil/ count
Resolution for the SeaOWLUV-A:	2.2 ppb crude oil/ count

The estimated limit of detection (LOD) for the ECO CDOM fluorometer is < 300 ppb crude oil (Conmy et al., 2014), i.e. 30 counts. Using the same count to LOD relationship, we estimate that the LOD for the

SeaOWL is < 67 ppb crude oil. Given improvements in the optics and electronics between the two instruments further investigation should demonstrate a lower effective LOD for the SeaOWL.

Caution should be exercised in using calibrations and LOD's from specific oils, injection methods and DOR's for a specific environment and oil. As with optical calibrations in regards to biogeochemical parameters such as chlorophyll concentration via fluorescence and absorption and total particulate concentration via backscattering and beam attenuation, the range of natural variability suggests that factory calibrations should at least be supplemented by co-located grab samples and regression analysis.



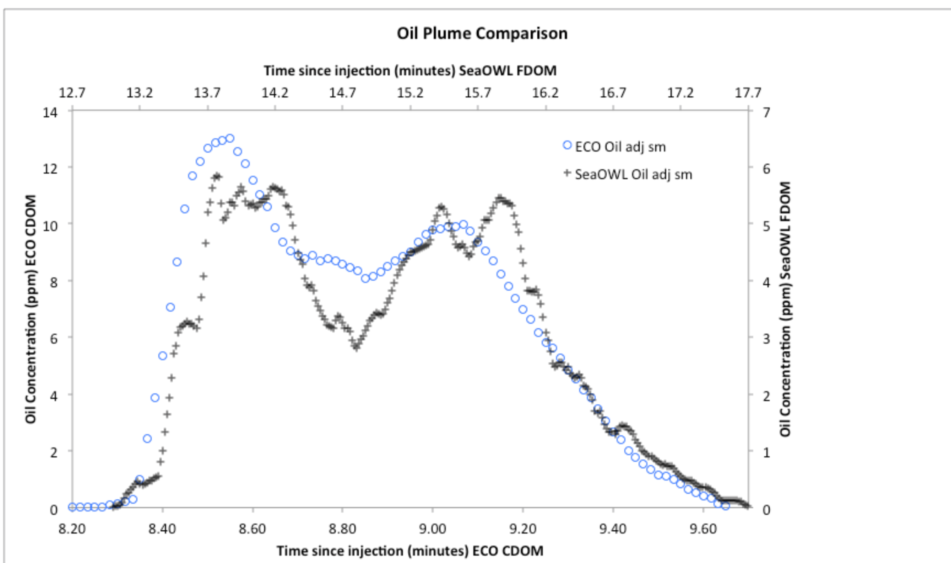


Fig. 1. Comparison of data from the ECO CDOM and SeaOWL in the COOGER facility flume using Arctic North Slope oil at a DOR of 1:20 (top panel) and 1:100 (bottom panel. Note the difference in scales between the two instruments and experiments.

III. MULTIPLE PARAMETERS:

Incorporating backscattering and chlorophyll sensors into the SeaOWL UV-A increases the ease of use and decreases the cost of providing the data. Backscattering in particular is useful to distinguish oil plumes of droplets and dissolved oil from waters with elevated dissolved organic matter from sources other than oil (e.g. sediments, phytoplankton).

Backscattering from oil droplets is a function of the particle size spectrum of the droplet field, with increased backscattering associated with smaller oil droplets on a backscattering per unit mass basis. The dispersant to oil ratio effects the droplet particle size distribution. The effect can be seen in Figure 2 where we compare the oil fluorescence signal and backscattering (as beta) for two experiments with a change in the dispersant to oil ratio from 1:100 to 1:20.

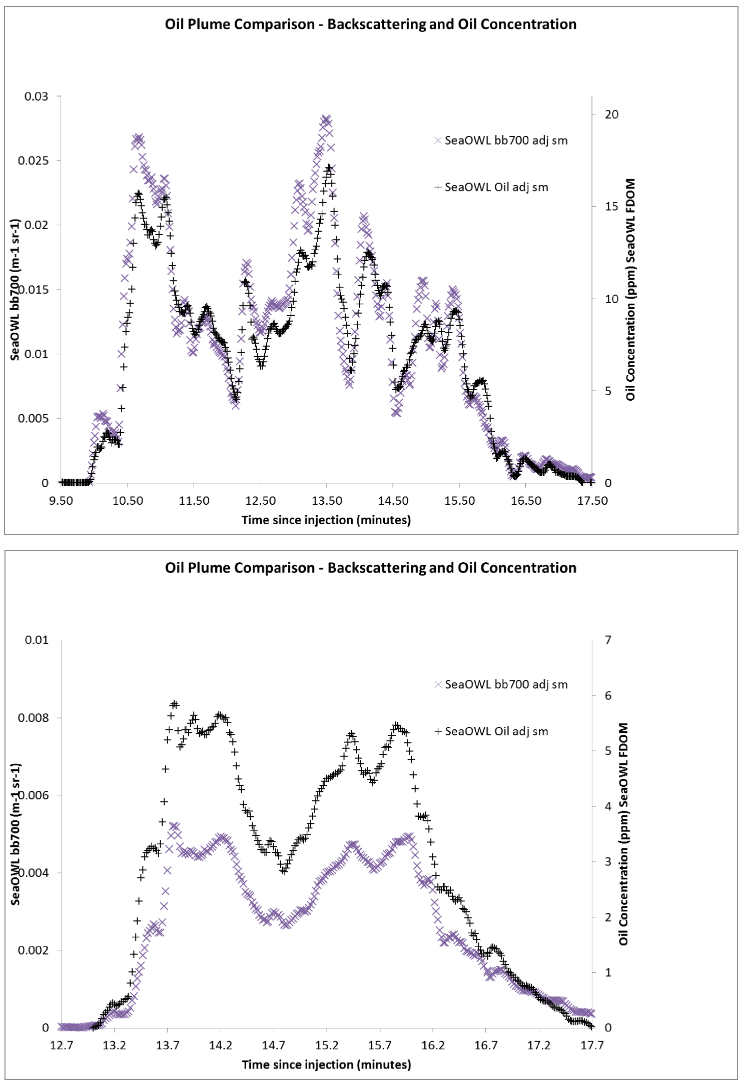


Fig. 2. Backscattering as beta and oil concentration from the SeaOWL UV-A instrument in the COOGER facility flume using Arctic North Slope oil at a DOR of 1:20 (top panel) and 1:100 (bottom panel. Note the difference in scales between the two instruments and experiments. The scales for the DOR 1:100 are one third that of the 1:20 chart.

IV. Fluorescent Intensity Ratio

In an event response environment management and resource allocation decisions are likely to be made by non-technical authorities on a time critical basis. Therefore, a technique that fundamentally requires further analysis post data collection is prone to be disregarded even if the data is ultimately proven to be indicative of the presence or absence of oil. Similarly, in an operating environment such as a producing field or for leak detection along a pipeline a sensor that presents all data as oil where the predominant signal in almost all cases is actually fluorescent dissolved organic matter (FDOM) is at best going to be ignored.

The fluorescent intensity ratio (FIR) has been used as a tool to quantify the effectiveness of dispersant use on an oil spill (Bugden et al., 2008). We have adapted this technique to overcome the overlap between oil and other sources of fluorescent dissolved organic matter (FDOM). Our conceptualization of the FIR is to use it as a time and space based measurement which changes as an oil plume ages from a droplet dominant to a droplet and dissolved mixture.

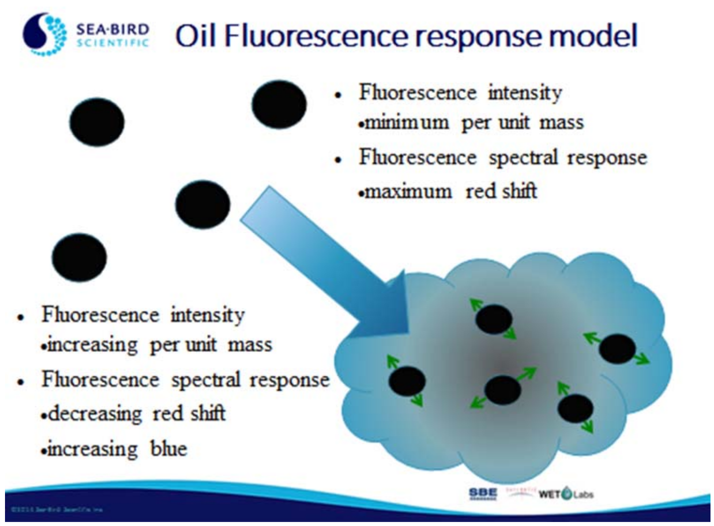


Fig. 3. Conceptual view of the oil fluorescence response model for an oil droplet particle field as it ages.

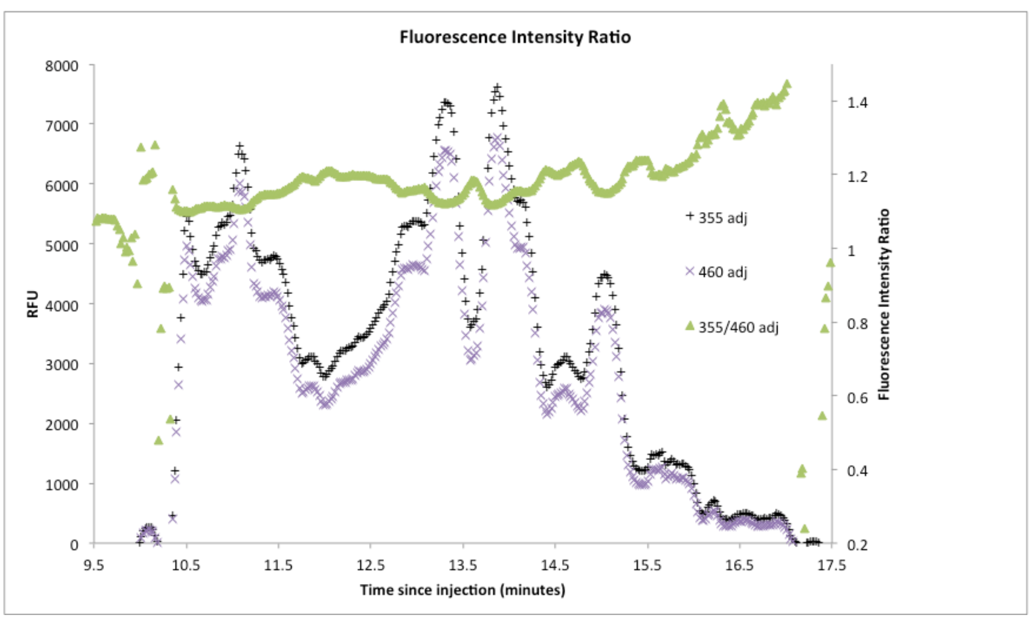


Fig. 4. Data from the Crude Oil WET Star 280/355 and 280/460 EX/EM channels during the passage of the plume overlaid by the FIR ratio. Data were adjusted by subtracting a background (pre-plume) average of sixty samples and smoothed with a running seven point centered average.

V. Conclusion:

Since the Deep Water Horizon event, there have been significant advancements in UV LEDs and subsequent development of new fluorescence sensors. These sensors use multiple excitation wavelengths and emission filters to more specifically target crude oil components (e.g. PAH's) and phases (dissolved and droplet). Combining response parameters from these sensors can be used to discriminate changes in the fluorescent dissolved organic matter (FDOM) concentration from crude oil, reducing the possibility of false positive signals. These new sensors, along with characterization of the flow field and basic physical and biogeochemical parameters in the near field and far field environments, can be combined to yield a robust methodology detecting sub-surface oil in natural waters.

Acknowledgement

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References

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