REAL TIME GEO-REFERENCED DETECTION OF DISPERSED OIL PLUMES

Christopher B. Fuller[1], James S. Bonner[1], Frank Kelly[1], Cheryl A. Page[2], Temitope Ojo[3]

The current SMART protocol used by the U.S. Coast Guard relies on traditional ex-situ fluorometers that require physical transport of the sample from the water column to the instruments. While sample transport methods are available (e.g. pumps and discrete sampling), they introduce time lags in the data acquisition process. These lags can be a source of error when the data is post analyzed and is not conducive to real-time monitoring efforts, creating significant logistical problems and dispersion (smearing) of the sample stream. Another limitation of the currently-used equipment is that it requires much attention to manually record GPS data which is later used to determine the spatial distribution of an oil plume. Recent developments of in-situ fluorometric instrumentation promise to simplify problems associated with deployment of ex-situ instrumentation (e.g. insuring that pumps are primed) in boat-based field applications. This study first compares the performance of two in-situ fluorometers in a simulated oil and dispersant application at the Shoreline Environmental Research Facility at Texas A&M University in Corpus Christi, Texas. The fluorometers were the WETStar and the ECP-FL3 (both by WETLabs, Inc.). To address issues related to data collection from a GPS and a fluorometer, a system was developed that simultaneously merges data from both instruments into a single file and presents the data real-time as a color-coded ship track. The applicability of this system was tested and evaluated during a spill response exercise conducted by the Texas General Land Office and the U.S. Coast Guard in Galveston Bay, Texas, U.S.A.

INTRODUCTION

Recent advances in technology have led to the development of small in-situ fluorometers. The relatively small dimensions of the units make them desirable for field applications. Previous laboratory experiments have shown that these small instruments respond well to chemically dispersed oil (Fuller et al., 2003). The fact that these instruments are deployed in-situ, simplifies deployment by alleviating problems associated with transporting samples to the detector. These advances promise to make in-situ instruments the device of choice for field applications.

SMART (Special Monitoring of Applied Response Technologies) is a guidance document, developed by several U.S. government agencies, that defines the protocols for the "rapid collection of real-time, scientifically based information" that would assist in the decision process required in oil spill dispersant applications (USCG, 2000). The current instrumentation recommended for use in the SMART protocol includes a field grade fluorometer with internal data logger, a Global Positioning System (GPS), and standard water sampling equipment. Also required by the SMART protocol is a team of technicians to set up the fluorometer (including pumps, hoses, etc) as well as to provide routine manual entries into a sampling log. However, implementation of these tasks on board a vessel at sea can be challenging. Experience has indicated problems maintaining a steady sample flow through the on-board fluorometer as well as difficulty in manually recording times, coordinates, and fluorometer readings.

These issues have led to the development of a the Multi-parameter Instrument Array and Control System (MPIACS) that simultaneously records the data from multiple instruments (i.e. fluorometer, GPS, CTD, LISST particle size analyzer) into a single data file while providing realtime visualization of data (Ojo et al., 2003a; Ojo et al., 2003b). While the MPIACS provides a comprehensive data acquisition package, it has many features not required or desired by spill responders (i.e. CTDs, spectrofluorometers, and particle size analyzers, tow cable requirements, etc.). These considerations have led to the development of a pared-down MPIACS unit with only a single in-situ fluorometer and a GPS for use by spill responders. This unit is named Biochemical Underwater Bay Analyzer (BUBA) Buster.

A primary objective of this study was to compare the applicability of two in-situ fluorometers in meso-scale conditions (i.e., in a wave tank) at the Shoreline Environmental Research Facility (SERF) in Corpus Christi, TX as part of an oil spill dispersant effectiveness evaluation. A secondary objective was to test the applicability of BUBA Buster in full field conditions during a spill exercise that used fluorescein dye to simulate the chemically dispersed oil (CDO) plume.

MATERIALS AND METHODS

Instrumentation

The Turner Designs 10-AU Field Fluorometer was configured with the 25 mm one-piece flow cell. For consistency with the SMART protocol, the fluorometer was configured to measure long wavelength oils with excitation light source, wavelength (_) = 300-400 nm light while an emission filter in front of the photodetector allows only fluorescence at 500 nm ± 100 nm to register.

The ECO-FL3 (WET Labs, Philomath, OR) is a newly-developed in-situ, multiple-wavelength fluorometer. Excitation wavelengths are 390 and 470 nm while emission wavelengths are 460, 530, and 695 nm. The instrument gives fluorescent responses to 3 specific Excitation/Emission pairs including a) chlorophyll A (EX 470/ EM 695), b) colored dissolved organic material (CDOM) (EX 370/EM 460), and c) fluorescein at (470/EM530). The

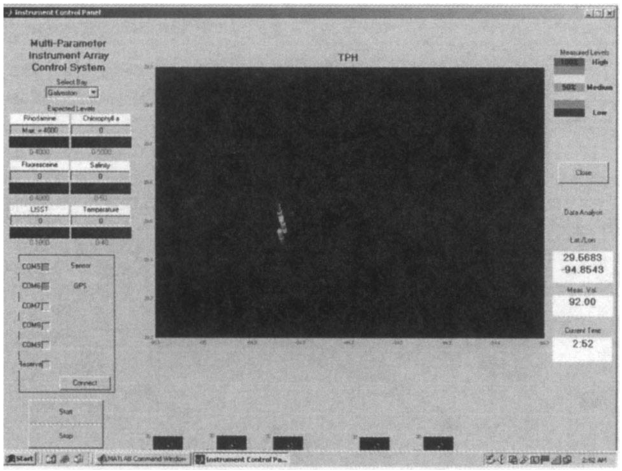
---

[1] Conrad Blucher Institute for Surveying and Science, Corpus Christi, TX, USA
[2] Texas Engineering Experiment Station, College Station, TX, USA
[3] Texas A&M University, College Station, TX, USA

CDOM channel uses emission and excitation wave lengths that are comparable to the wavelength used by the Turner 10-AU for oil detection. Therefore, the CDOM channel was selected as the appropriate parameter to monitor for dispersed oil concentrations.

The WETStar (WET Labs, Philomath, OR) is a single channel in-situ fluorometer with a flow cell that measures the fluorescent response to CDOM (EX 370/EM460). The WETStar utilizes a flow cell that requires a continuous flow. So field use of the instrument necessitated that the instrument be towed through the water to provide continuous flow.

BUBA (Biochemical Underwater Bay Analyzer) Buster is a user-friendly unit that includes: 1) a newly-developed submersible fluorometer (WETStar; solid-state device; no field calibration required); 2) a GPS unit that allows for spatial stamping of the data; and 3) software for visualization of the real-time data. The BUBA Buster simultaneously merges the NEMA data stream from the Garmin GPS with the fluorescence (text) data stream from the WETStar. The data visualization capacity of BUBA Buster is demonstrated in Figure 1. This figure presents a captured screen depicting a simulated ship track through a simulated oil plume.



Select Bay: Galveston
Rhodamine: Max = 4000
Chlorophyll a: 0
Fluorescene: 0
Salinity: 0
LISST: 0
Temperature: 0
COM5: Sensor
COM6: GPS
Lat./Lon: 29.5683 -94.8543
Meas. Val: 92.00
Current Time: 2:52

FIGURE 1 SIMULATED SHIP TRACK THROUGH DISPERSED OIL PLUME GENERATED WITH BUBA BUSTER

Meso-scale Testing

The Eco-FL3 and the WETStar (in the BUBA Buster configuration) fluorometers were compared in a meso-scale (wave-tank) environment. The testing was conducted at the Shoreline Environmental Research Facility (SERF) in Corpus Christi, Texas, USA. The meso-scale facility includes nine wave tanks measuring 33.5 m (length) by 2.1 m (width) x 2.4 m (depth). Each tank is equipped with a computer-controlled wave board that can produce variable wave patterns and feedback circuits to automatically control the tidal range and cycles. Sea water used in the facility is taken from the adjacent waters of the Laguna Madre. More details of the facility are discussed in Kitchen et al.(1997).

A known mass of oil (5.1 kg) was applied to the water surface under quiescent conditions. Prior to the oil application, waves were produced for one hour to achieve steady state conditions with respect to ambient suspended solids. Air booms at either end of the tank were used to maintain the position of the slick in the center of the tank. The dispersant was applied using a calibrated, four nozzle spray system mounted on a motorized bridge (dispersant to crude oil ratio of 1:10). The wave regime was restarted immediately after the dispersant application and continued until the experiment was terminated. Sub-surface water column samples were collected periodically from 3 locations in the tank at depths of 0.5 ft (0.15 m) and 3 ft (0.91 m).

The BUBA Buster was deployed at 0.91 meter depth and suspended from a motorized bridge that allowed for continuous flow through the WETStar's flow cell. The ECO-FL3 was suspended from a second bridge that was manually moved to different tank locations. Target sensor depth was obtained by lowering or raising the instrument to respective mark on the tether line.

The tank conditions were designed to simulate a shallow embayment (no sandy substrate). In place of a sand beach, the wave tank has been modified with a concrete wave dissipater with a parabolic profile to minimize wave reflection. Additionally, the wave dissipater has been sealed with an elastomeric liner to minimize oil adsorption. Scaling with both Froude and Energy Density analyses permitted simulation of environmentally-relevant wave conditions for dispersant effectiveness testing (Bonner et al., 2003). The wave height was 0.12 m (0.4 ft), the wave period was 1.25 seconds, still water depth was 1.8 m (6ft). The parameters were selected to simulate wave conditions comparable to Corpus Christi Bay. By design, the experiment was run in batch mode (i.e. no tidal simulation, constant volume).

Artificially-weathered Arabian medium crude oil was used for this demonstration. The weathering process was simulated by sparging the oil with nitrogen at 105º F. This process reduced the oil volume by about 25%.

Corexit 9500 (manufactured by Nalco/Exxon) was the selected dispersant. It is reported to have increased effectiveness and similar toxicity to its predecessor Corexit 9527 (Blondina and Sowby, 1997; Singer et al, 1996; Varadaraj et al, 1995).

The water column was sampled in three locations: near the wave board (WB), near the wave dissipater (WD), and mid-tank (MT) (under the slick). At each location, samples were collected at two depths (0.15 m and 0.91 m). Water column sampling was conducted at the following times: pre-oil baseline, t= 0.5 hours, and t= 1 hour (where time of dispersant application was defined as t=0 hours). These samples were taken immediately adjacent to and simultaneously with ECO-FL3 fluorometer sampling. The aqueous samples were acidified to pH 2 using HCl and refrigerated at 4º C until processed.

Water column samples were extracted using a solid-phase extraction procedure (SPE) procedure (EPA SW846, method 3535). Each aqueous sample was passed through a pre-conditioned SPE disk designed to attract hydrophobic compounds. The disk was then extracted with dichloromethane (DCM) to transfer the contaminants into the organic solvent. Aliquots of the DCM extracts were subjected to GS-MS analysis to determine total petroleum hydrocarbon concentrations as described in Mills et al. (1999).

Field Testing of BUBA Buster

On August 26, 2004 the Texas General Land Office, in cooperation with the U.S. Coast Guard and Clean Channel Association, conducted a spill/dispersant simulation in Galveston Bay, TX (N 29º22'40", W 94º22'07"). The initial spill was simulated by applying 1.1 kg (40 oz) of fluorescein dye (Orion Safety Products, Peru, IN)) at the pre-determined spill location. Following dye application, the simulated dispersant was applied to the dye plume via an Ag-Tractor, operated by Lane Aviation, Rosenberg, TX. Rhodamine dye (7.56 L mixed in 378 L of water) was used to simulate the dispersant. The entire volume of rhodamine dye was applied to the simulated oil plume during several low-altitude passes of the air craft.

Two fluorometers (Turner 10AU and a WETStar/BUBA Buster) were used to monitor the dye plume (i.e., the fluorescein dye concentrations). Baseline fluorometer samples were collected well outside the visual plume area. Once the dye was applied, the vessel made several passes through the plume at a speed of 2-4 knots with the fluorometers deployed at the target depth (1 meter).

Data from the Turner 10AU fluorometer was manually recorded, while automatic data logging and data visualization were presented in real-time with the BUBA Buster unit.

RESULTS

Mesoscale Testing (SERF Wave Tank)

Fluorometer results from the wave tank test are shown as in Figures 2 and 3. These figures present the TPH concentrations as a function of time for both the WETStar and ECO-FL3. The TPH values were determined using equations derived from the linear regressions of the chemically dispersed oil response curves. All TPH values reported have been corrected for background fluorescence (i.e. the background fluorescence was subtracted prior to calculation).

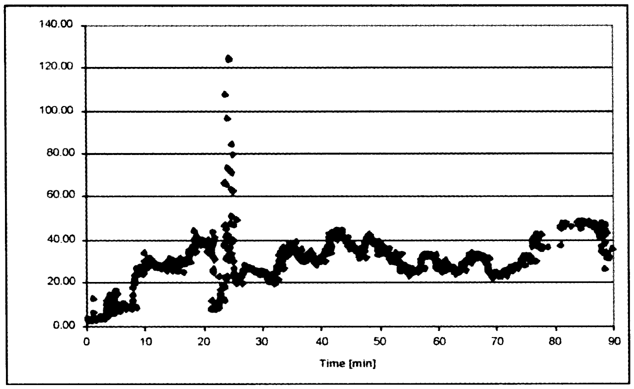


FIGURE 2 BUBA BUSTER (WETSTAR) MEASUREMENTS OF CHEMICALLY DISPERSED OIL IN THE SERF WAVE TANK

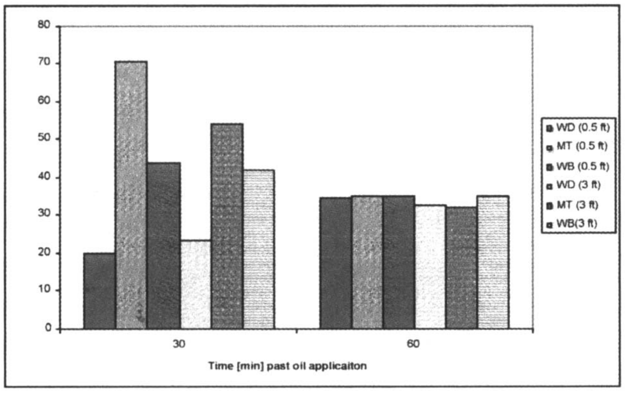


FIGURE 3 ECO-FL3 MEASUREMENTS OF CHEMICALLY DISPERSED OIL IN SERF WAVE TANK

Figure 2 shows the corrected TPH [nominal oil load] values determined by the WETStar. The peaks correspond to times when the fluorometer was towed through the center of the dispersed oil plume. Figure 3 shows the oil concentration, measured with the ECO-FL3, at the various tank locations (with respect to depth and longitudinal tank position) from the two sampling events at 30 and 60 minutes post dispersant application. Inspection of these figures indicates the heterogeneity of the dispersed oil plume in the wave tank at t = 30 min. This is indicated by the spike of 130 mg/L detected by the WETStar at 25 min (Fig.2) and the maximum value of 70 mg/L detected by the ECO-FL3 at 30 min at MT 0.5 ft (Fig. 3). At 1 hour, the ECO-FL3 indicates that the plume is nearly homogenous through the upper 1 meter of water column through out the wave tank. Comparison of the two figures also shows good agreement between the ECO-FL3 and WETStar as indicated by the values about 30 mg/L at 1hour from both instruments.

Direct comparison of values from both instruments is not justified as the water volumes sampled in each case are not identical due to samples being collected at slightly different times. This discrepancy is due to the operational requirement that the WETStar be towed to collect a sample. While the towing was accomplished using a motorized bridge it was not possible to collect samples from both instruments at the same time.

GC/MS analysis of discrete water samples allowed correlation of the ECO-FL3 fluorometric response to standard laboratory methods for petroleum hydrocarbons. Results from this comparison (Figure 4) show a good correlation (R^2=0.9155) between the ECO-FL3 raw fluorescence and total petroleum hydrocarbon (TPH) concentration measured by GC-MS. This result demonstrates the ability of the in-situ fluorometer to quantitatively measure water column hydrocarbon concentrations. Furthermore, it shows that the instrument is capable of providing oil concentration values that are comparable to established laboratory methods, assuming that the appropriate response factors are generated prior to deployment (i.e. response curves).

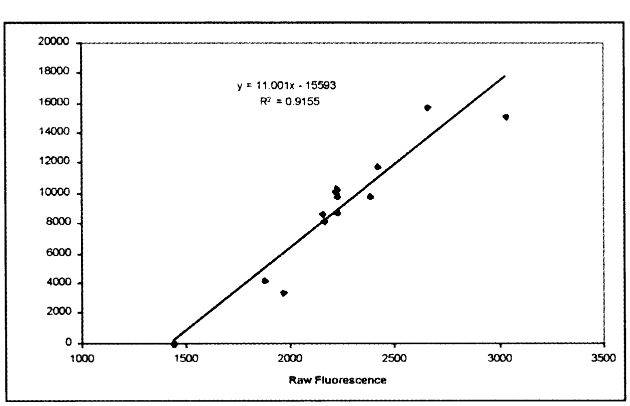


FIGURE 4. ECO-FL3 VERSUS GC-MS ANALYSES. NOTE: THE X-AXIS INDICATES RAW FLUORESCENCE AS MEASURED BY THE ECO-FL3, WHILE THE Y-AXIS INDICATES TPH AS QUANTIFIED BY GC-MS.

Field Testing

The responses from both the Turner 10AU and BUBA Buster (WETStar) are shown as a function of time in Figure 5. Fluorescein concentration values shown for both instruments have been corrected for background fluorescence (i.e. baseline fluorescence readings taken prior to the dye application (time= 09.2 hours) were subtracted from readings). The peaks in this figure clearly indicate when the fluorometers were inside the plume while the lower readings are indicative of locations outside of the plume. Coupling the concentration and GPS position data would allow the extent of the plume to be characterized. However, completion of that task is outside the scope of this work. Manual concentration records from the Turner 10-AU are sparse. However, use of the data logger could have improved data resolution.

Discreet baseline samples were also collected during the exercise. Upon returning to the laboratory these sample were reanalyzed with the Turner and BUBA Buster/WETStar. These samples were then spiked with a known concentration of fluorescein dye. Results from this laboratory post check indicated that the Turner 10AU and BUBA Buster/WETStar readings were within 1.02 and 0.78 of the actual spiked concentration, respectively.

Using these values, the CDOM WETStar readings shown in Figure 5, were corrected by dividing the raw WETStar concentration values by 0.778. After correction, the agreement between the BUBA Buster/WETStar and the Turner 10AU is visibly improved as shown by selected corrected WETStar values in Figure 5.

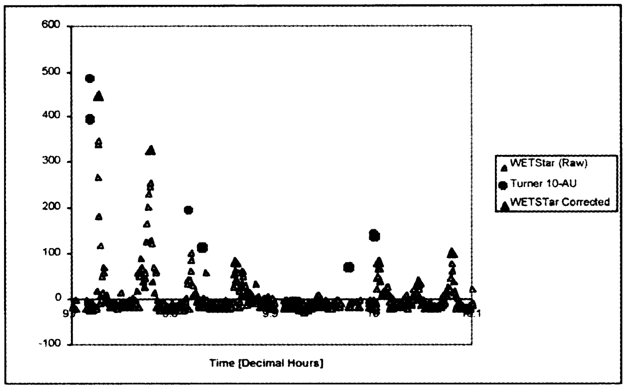


FIGURE 5 COMPARISON OF WETSTAR AND TURNER 10-AU FLUORESCEIN RESPONSE

CONCLUSIONS

Results from these exercises demonstrate that in-situ fluorometers are suitable for use in spill detection applications with respect to their ability to detect parameters of interest (i.e. chemically dispersed oil) under true environmental conditions. The integrated system (BUBA Buster) was shown to reliably collect geo- and time-referenced concentration data with great resolution. Furthermore, the compact size and ease of reliable deployment will surely be appreciated by the end user, especially when used under the inclement conditions expected during a true spill condition.

ACKNOWLEDGEMENTS

We would like to acknowledge Robin Jamail and the Texas General Land Office for their support of this research.

REFERENCES

Blondina G.J. and Sowby M.L. (1997) Comparative efficacy of two Corexit(r) dispersants as measured using California's modified swirling flask test. In Proceedings of the Twentieth Arctic and Marine Oilspill (AMOP) Technical Program. Environment Canada, Ottawa, Ontario, 1, pp. 561-573.

Bonner, J., Page, C., Fuller, C. "Meso-Scale Testing and Development of Test Procedures to Maintain Mass Balance" Marine Pollution Bulletin (2003): 47 (9-12), 406-414

Fuller, C.B., Sterling, M.C., Bonner, J. S., Ojo, T., Page, C.A. "Field Instruments for Real Time In-Situ Crude Oil Concentration Measurements" Proceedings of the Twenty-sixth Arctic and Marine Oilspill Program (AMOP) Technical Seminar. Environment Canada, Ottawa, Canada, Vol 2 (2003): 755-764.

Kitchen, R. B., Bonner, J.S., Autenrieth, R.L., Donnelly, K.C., Ernest, A.N.S., "Introducing COSS: A New and Unique Oil Spill Research Facility," *Proceedings of the Twentieth Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, Vol. 2, No. 20, pp 1327-1407, June 1997.

Mills, M.A., McDonald, T.J., Bonner, J.S., Simon, M.A., and Autenrieth, R.L., "Method for Quantifying the Fate of Petroleum in the Environment." *Chemosphere* 39(14): 2563-2582, 1999.

Ojo, T., Sterling, M.C., Bonner, J.S., Fuller, C.B., Kelly, F., Page, C.A. (2003a)."Multi-Parameter Instrument Array and Control System (MPIACS): A Software Interface Implementation Of Real-Time Data Acquisition and Visualization of Environmental Monitoring" Proceedings of the Oceans 2003 Marine Technology and Ocean Science Conference, San Diego, CA, Sept 22-25, 2003, on CD-ROM. (2003) (PDF 143 KB)

Ojo, T., Bonner, J. S., Page, C.A., Sterling, M.C., Fuller, C.B., Kelly, F. "Field Simulation Experiment of Aerial Dispersant Application for Spill of Opportunity" Proceedings of the Twenty-sixth Arctic and Marine Oilspill Program (AMOP) Technical Seminar. Environment Canada, Ottawa, Canada, Vol 2 (2003b): 813-824.

Singer M., George S., Jacobson S., Lee I., Weetman L., Tjeerdema R. and Sowby M. (1996) Comparison of acute aquatic effects of the oil dispersant Corexit$^{(r)}$ 9500 and those of other Corexit® series dispersants. Ecotoxicol. Environ. Saf. 35, 183-189.

U. S. Coast Guard (USCG), Special Monitoring of Applied Response Technologies, USCG Headquarters homepage: http://www.uscg.mil/vrp/reg/smart.shtml, 55 p, 2000.

Varadaraj R., Robbins M.L., Bock J., Pace S. and MacDonald D. (1995) Dispersion and biodegradation of oil spills on water. In Proceedings from the 1995 Oil Spill Conference. American Petroleum Institute, Washington, DC, pp. 101-106.