Fluorescence-estimated Oil Concentration (F_{oil}) in the *Deepwater Horizon* Subsea Oil Plume

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EXTENDED ABSTRACT

Expedient oil spill emergency response efforts require the ability to sufficiently detect, track and map spilled oil in aquatic environments. Fluorescence as a spill monitoring tool for submerged (non-floating nor sunken) oil is widely accepted and has been used for over 40 years. U.S. SMART (Special Monitoring of Applied Response Technologies) protocols use real-time fluorescence monitoring during surface dispersant operations. Such monitoring requires rapid, reliable, easy-to-operate *in situ* fluorometers.

Submerged oil surveillance and sample collection becomes increasingly challenging for oil releases within deep waters. The 2010 Gulf of Mexico *Deepwater Horizon* (DWH) spill tested the limits of submerged oil spill surveillance. Response efforts proved challenging due to depth and duration of the release (1500 m and 87 days), inability to visually inspect subsea oil, heterogeneity of the plume, and coarse grab sampling with non-detects insufficient to capture its magnitude and extent. Thus, responders were more reliant on submersible sensors in lieu of visual observations to provide critical tracking measurements of oil between 900 - 1600 m over the large temporal-spatial extent. The submerged plume was identified based on fluorescence, light scattering, acoustics and concentrations of specific petroleum hydrocarbons. Comparatively, fluorescence was the most widely used technique to track the plume from 22 monitoring vessels as fluorometers were readily available, collected real-time measurements,

and easily deployed and interpreted. Prior to DWH, *in situ* fluorescence in spill surveillance was primarily qualitative, used for presence or absence, or relative oil amounts. DWH demonstrated the need to examine whether *in situ* fluorescence sensors could be used quantitatively, where detections limits for Commercial-Off-The-Shelf (COTS) fluorometers can measure oil concentrations as low as 300 ppb.

The objective of this analysis was to develop an approach to intercalibrate mined *in situ* fluorescence data collected via vertical profilers (n=1,157) from numerous ECO-FL fluorometers (Sea-Bird Scientific WET Labs, Inc.; Philomath, OR) deployed from vessels during DWH (BP Gulf Science Data, 2018; 2019). During monitoring efforts, discrete grab samples for chemical analyses provided a coarse picture of the oil plume footprint, but the majority of the subsea samples were below standard analytical detection limits for petroleum hydrocarbons (n=17,164 collected, n=7,665 above detection limit). Here we synthesized millions of continuous fluorescence data points from hundreds of contemporaneously discrete samples collected from May - October 2010. Data were geographically and temporally aligned to provide direct comparisons and demonstrate that fluorescence-estimated oil concentration (F_{oil}) can be used to supplement discrete samples of Total Polycyclic Aromatic Hydrocarbons (TPAH50) or Benzene-Toluene-Ethylbenzene-Xylene (BTEX) concentration. Data mined from Gulf Science Data repository were well correlated, and geographically and temporally aligned to provide direct comparisons. Described will be the methods to intercalibrate the datasets and to visually approximate the 3-D geographic extent of the oil plume.

This approach expands the number of quantitative hydrocarbon concentration data points by supplementing discrete bottle samples with continuous optical proxy data. This in turn increases the number of ground-truth observations available as input parameters and validation for transport models and for evaluating monitoring strategies, spill impacts and damage assessment. F_{oil} yields oil mapping with finer temporo-spatial resolution not achieved through coarse discrete measurements alone. Forward-looking, this approach and these results are promising for future spill emergency response. Fluorescence can be measured from a range of sampling platforms from simplistic profilers to sophisticated AUVs. This offers flexibility for oil monitoring both in a typical small-scale spill, as well as in atypical large-scale incidents. Furthermore, data is easily digested into common operating platforms for time critical decision-making during emergency response operations. Globally, current offshore oil production deeper than 125 m accounts for about 30% of total oil production, making it ever apparent that deep submerged oil plume tracking requires reliable sensors with real-time capabilities.