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Advances in Underwater Oil Plume Detection Capabilities

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ABSTRACT

Historically, visual observation is an emergency responder's first 'tool' in identifying spilled oil. Optical detection has since expanded to include a myriad of signals from space, aircraft, drone, vessel and submersible platforms that can provide critical information for decision-making during spill response efforts. Spill monitoring efforts below the air-water interface have been vastly improved by advances with *in situ* optical sensors and vehicle platform technology. Optical techniques using fluorescence, scattering, and holography offer a means to determine dissolved versus droplet fractions, provide oil concentration estimates and serve as proxies for dispersion efficiency. For subsurface spills over large space and time scales, Autonomous Underwater Vehicles (AUVs) can be used to provide subsurface plume footprints and estimate oil concentrations. For smaller, more frequent spills, tethered compact Remotely Operated Vehicles (ROVs) may be more appropriate as they are easy to deploy for rapid detection.

Two underwater oil detection technologies have been developed: (1) A Remote Environmental Monitoring UnitS (REMUS-600) AUV equipped with fluorescence and backscatter SeaOWL UV-A (Oil-in-Water Locator; Sea-Bird Scientific WET Labs Inc.), holographic imager (HoloCam; SeaScan, Inc), hydrographic information, video camera, CTD and a water/oil sampler. (2) A tethered ROV system (DTG2, Deep Trekker Inc.) equipped with video camera, UviLux (Chelsea Technologies Group, Inc) fluorometer, a CTD and water/oil sampler. Calibration and validation tests of the sensor suite were conducted at the Coastal Response Research Center flume tank (NH, USA). Oil concentration estimates were verified by chemical analysis of hydrocarbons and particle size analysis (LISST 200X, Sequoia, Inc). Operational performance of the ROV platform and sensors was evaluated at the Ohmsett wave tank (NJ, USA). Field performance of the REMUS and sensor suite was evaluated at natural seeps near Santa Barbara, CA. This research demonstrates the forensic value of *in situ* optical data for improved understanding of the behavior and transport of spilled oil below the air-sea interface.

INTRODUCTION

Oil detection is essential for spill response decision-making, environmental impact assessments as well as understanding the ultimate fate of oil. The 2010 *Deepwater Horizon* (DWH) oil spill highlighted knowledge gaps with respect to rapid *in situ* monitoring for decision-making, where the spill proved challenging in part due to the inability to visually inspect the subsea oil plume (NOAA Technical Report No.24, 2011). This emphasized the need for further development of *in situ* sensing systems that can inform the early response efforts (White et al., 2016).

A variety of oil detection techniques were employed during DWH to assess the spatial extent, quantify the release, and characterize the chemical composition of the spilled oil. Subsurface oil and gas detection were conducted via *in situ* sensors deployed on surface vessel, buoy, profiler, glider, remotely operated vehicle (ROVs), autonomous underwater vehicle (AUVs) and manned vehicle platforms. Forensic sensors mounted with CTD (Conductivity-Temperature-Depth) packages included membrane inlet mass spectrometers (MS) to detect dissolved hydrocarbons (Camilli et al., 2010; Reddy et al., 2012), fluorometers to detect polycyclic aromatic hydrocarbons (dissolved and small particulates) (NOAA Technical Report No.25, 2011; Conmy et al., 2014), beam transmissometers to detect suspended particulate matter, digital holographic cameras (Li et al., 2015) and particle size analyzers (Li et al., 2009) measured the oil droplet size distribution, and dissolved gas sensors. In the wake of the spill questions remain regarding sensor and platform applicability (selectivity, sensitivity, certainty) for oil detection, quantification and fate. Evaluating the operational nature of the best-available technologies serves to identify which potential spill response decision-support tools are akin to a Technical Readiness Level of 8-9 (Mankins, 1995; Panetta and Potter, 2016).

AUVs overcome constraints and logistical challenges encountered with tethered data collection platforms and airborne or surface-based methods (Kukulya et al., 2016). These systems can provide rapid in situ detection of spilled oil at fine spatial and temporal scales (Camilli et al., 2010; Ryan et al., 2011). AUVs offer the added benefit in being able to collect measurements under adverse weather conditions, in remote locations, where deployments can last days and continuously send data during missions (Bellingham et al., 2008; Kaminski et al., 2010; Kukulya et al., 2010). One such system is the propeller-driven REMUS-600 (Remote Environmental Monitoring UnitS) which has been recently outfitted with a suite of sensors ideal for quantifying and characterizing oil in the water column. Commercial-off-the-shelf (COTS) sensors for CTD, dissolved oxygen, oil fluorescence and optical backscatter (OBS), and video have been coupled with a customized holographic imager (Davis and Loomis, 2014) and discrete oil/water sampling capabilities. AUVs equipped with these capabilities can be strong assets for spills over large space and time scales, where the sensors provide for measuring dissolved and particulate hydrocarbons, oil droplet size distribution and gas bubbles. In contrast, small, inexpensive, light-weight tethered ROV units equipped with CTD, fluorescence, video and discrete sampling capabilities offer the ability to detect oil plumes over fine spatial scales. These portable, easy-to-use systems are ideal during small, more frequent spills, requiring 1-2 persons to deploy and operate.

Presented here are results from REMUS-600 AUV and Deep Trekker ROV sensor calibration and validation tests conducted at the Coastal Response Research Center flume tank (NH, USA). Oil concentration estimates were verified by chemical analysis of hydrocarbons and particle size analysis to validate fluorescence, optical backscatter and holographic data. Operational performance of the ROV platform was evaluated at the Ohmsett wave tank (NJ, USA). Field performance of the REMUS-600 was evaluated at natural seeps near Santa Barbara, CA. This research demonstrates the forensic value of *in situ* optical data for improved understanding of the behavior and transport of spilled oil below the air-sea interface. It is responsive to needs elevated within spill planning activities, such as the proposed decision-rule amendments to the US federal government 40 CFR § 300.900-920 Subpart J for spill monitoring requirements under the National Oil and Hazardous Substances Pollution Contingency Plan. Efforts presented here are aligned with ongoing science and methods development activities by federal trustees to advance technologies for oil spill preparedness and protecting aquatic resources.

METHODS

UNH Flume Tank – Prior to operational field and wave tank testing, performance of *in situ* optical sensors was evaluated during oil dispersion experiments within the University of New Hampshire Coastal Response Research Center (CRRC) circulating flume tank (Gloekler et al., 2017). Stepwise additions of Hoops crude oil (25 – 200 ml volumes) were added to the tank via a large syringe system. Optical sensors were placed in series inside the tank and within the path of the dispersed plumes (Figure 1a). Sensors continuously collected measurements during the oil additions and discrete bottle samples were collected periodically for chemical analyses.

Fluorescence and Optical Backscatter Analysis – The SeaOWL UV-A (Oil-in-Water Locator; Sea-Bird Scientific WET Labs Inc.) uses three wavelength pairs to measure simultaneously dissolved hydrocarbons (fluorescence; FDOM), oil droplets (optical back scatter; OBS) and chlorophyll (CHL). It was produced specifically for autonomous platforms, and offers 5x the optical resolution than its predecessor, the ECO fluorometer (Excitation/Emission (Ex/Em) λ = 360/470 nm) capable of reliably sensing dissolved hydrocarbons at low concentrations during the DWH spill and in wave tank testing (Conmy et al., 2014). The UviLux (Chelsea Technologies Group, Inc.) fluorometer has wavelengths centered on Ex/Em = 255/365 nm. Established methods for blank subtraction, and conversion to quinine sulfate dihydrate Equivalents (ppb QSE) were followed as outlined in the manufacturer's manual and calibration sheet.

Particle Size Analysis – The digital holographic imager, HoloCam (SeaScan, Inc.) captures three-dimensional (3D) holographic images of a volume of water between two probes, that can be used to estimate oil droplet concentration, shape, and size and opacity. The HoloCam measures oil droplets and plankton ranging µm to cm sizes and the miniaturized system makes it amenable to deployment on AUVs. The images of particles and plankton are extracted with sufficient resolution to distinguish major plankton taxa, oil droplets and bubbles (Loomis, 2011). Image processing was via methods developed by WHOI (*Fischell, pers. comm.).*

A Laser *In Situ* Scattering and Transmissometry probe (LISST-200X, Sequoia Scientific, Inc.) was used to measure Droplet Size Distribution (DSD) from 1.25 to 500 µm, Mean Diameter

(MD) and Total Volume Concentration (TVC) within the CRRC flume tank experiment. Measurements were collected continuously during oil releases, where DSD, MD, and TVC for each treatment was summarized and reported.

Oil Chemistry – Discrete oil in water samples were analyzed for monoaromatic hydrocarbons (i.e., benzene, toluene, ethylbenzene and xylene; BTEX), polycyclic aromatic hydrocarbons (PAHs), alkanes (C10-C35 normal aliphatics, and branched alkanes [pristine and phytane]) and total petroleum hydrocarbons (TPH; as total extracted petroleum hydrocarbons). PAHs analyzed included 2-4 ring compounds and their alkylated homologs. Concentrations of the detected alkanes and PAHs were summed to compute total alkane and PAH concentrations, respectively. BTEX measurements were performed using an Agilent 7890A Gas Chromatograph (GC) with a 5975C mass selective detector (MSD) following EPA Method 524.3 modified to perform head space analysis instead of purge and trap. For PAHs and alkanes measurements, samples were extracted with dichloromethane and quantified using an Agilent 6890N GC with an Agilent 5975 MSD following EPA Method 8270D. The DCM extracts were also quantified for TPH on an Agilent 7890B GC equipped with a flame ionization detector (FID) following EPA Method 8015B.

REMUS-600 Field Test - A REMUS-600 vehicle (600 m depth rating) was deployed in waters off the coast of Santa Barbara, CA in August 2019 from the USCGC *George Cobb* (WLM-564) (Figure 1b). The REMUS-600 was configured with the SeaOWL UV-A sensor to detect dissolved and particulate fractions of oil. The HoloCam imager was mounted in the nose of the vehicle with protruding probes to discern oil from other particulates and estimate concentrations. A forward-facing GoPro Hero 3 video camera captured continuous video, allowing for visible assessment of the water column. In addition to oil characterization sensors and capabilities, the vehicle was outfitted with the following instrument capabilities: iridium, WHOI micromodem acoustic communications (ACOMMS), a 1,200-kHz up/down ADCP (Acoustic Doppler Current Profiler),a PHINS inertial navigation system (INS, modelC7), a NBOSI CTD, an AADI dissolved oxygen probe, anda Licor photosynthetically active radiation (PAR) sensor.

The REMUS-600 includes a modular oil/water gulping system (i.e., the Gulper) designed by WHOI to complement *in situ* measurements. Twelve 1-Lglass bottles can be stored within the vehicle. A multiport manifold connects the valve and bottles, reducing the need for tubing and potential cross contamination. AUV behaviors, developed by WHOI, dictate timing and location of discrete sample collection via the Gulper: the “Circle/Spiral/Gulp” and the “Point and Gulp” Behaviors. The former is an adaptive behavior that interrupts the vehicle when it finds something of interest. If the vehicle encounters elevated fluorescence intensity, it would return to the location of the highest value to collect a discrete sample using a circular search pattern. This behavior is best suited for exploratory missions, where operators are unsure of oil location and/or concentration in the water column. The “Point and Gulp Behavior” in a non-adaptive behavior and therefore requires all the planning of the mission to occur prior to the start of the mission. This behavior is used when a specific latitude, longitude, and depth are desired for sampling.

Data streams from REMUS sensors were delivered to a ship-based computer in near real-time (holographic images were downloaded when on ship). Data were loaded into the NOAA Data Integration, Visualization, Exploration and Reporting (DIVER) data warehouse utilizing the standard electronic data deliverable format facilitating data visualization and mapping in NOAA’s Environmental Response Management Application (ERMA®) common operational platform.

Deep Trekker ROV Ohmsett Test - Testing of a small, light-weight tethered mini observation-class underwater ROV (DTG2, Deep Trekker Inc.) took place at the Ohmsett wave tank. The sensor suite and bottle sampler were configured by Water Mapping, Inc. The DTG2 is rated to max 200 m depth and capable of navigating, transmitting UviLux fluorometry data, and collecting 360^{o} vertical real-time video which is displayed and stored on the pilot's controller to help identify plumes (Figure 1c and 1d). Real time navigational data include heading and depth; additionally, salinity, temperature, and turbidity data are stored on externally mounted HOBO data loggers. The ROV is adapted to carry either a single or dual 1-L sampler for collecting oil based on fluorometry or when the pilot observes a feature of interest on the real-time video.

RESULTS & DISCUSSION

Flume Tank Sensor Performance Evaluation – SeaOWL UV-A fluorescence and OBS exhibited linear response to Hoops Crude oil additions within the flume tank (Figure 2, top). Sensor maximum intensity within the oil plume for each oil addition was recorded and regressed to oil volume. Similarly, UviLux fluorescence and LISST 200X Total Volume Concentration (Figure 2, bottom) also exhibited linearity over the applied concentration range. Droplet Size Distribution for three oil volumes show sufficient physical dispersion, where median droplet size decreased with increased oil volume due to continual dispersion/dissolution of droplets from the prior oil additions (Figure 3). Number of oil droplets per frame measured by the HoloCam is positively correlated with LISST TVC (R^2=0.8997).

ROV Ohmsett Test – The tethered ROV vehicle test in the wave tank demonstrated its utility at providing subsurface oil detection and oil concentration estimates. A time series of fluorescence intensity (Figure 4) in conjunction with recorded video and discrete sample collection serve as converging lines of evidence to confirm the presence of oil. A grab sample collected from the ROV at a time point close to the latter fluorescence peak in Figure 4 exhibited TPH value of 2.03 mg/L, total PAH of 83.39 µg/L, and BTEX of 1129 µg/L.

REMUS-600 Field Test - The ocean consists of a variety of dissolved and particulate materials suspended in the water column (plankton, detritus, sediments, organic matter, etc). These materials absorb and scatter wavelengths of light, which is dependent on chemical (molecular bonds) and physical nature (size and shape) of the material. Some materials (pigments, proteins, FDOM-fluorescent Dissolved Organic Matter, petroleum oils) also produce fluorescence. Regions of the ocean have ambient concentrations of FDOM that can be predictable based on conservative mixing and hydrographic knowledge. In Santa Barbara coastal waters, there are limited freshwater sources of FDOM entering the ocean. Thus, salinity is high and background FDOM fluorescence is predictably stable at ~2 ppb QSE in deeper waters down to 35 m, with slightly higher concentrations in the surface waters. Deviations from these concentrations indicate sources of new fluorescent material, such as petroleum hydrocarbons.

Of the 19 REMUS-600 mission runs near the Santa Barbara seeps, highlighted here are two examples to demonstrate its utility for oil detection. The first is the detection of oil at 35 m depth via elevated signatures in fluorescence and OBS exhibited on mission (MSN) 3 (Figure 5, red symbols). These anomalies located southwest of the Coal Point area are not the result of biological productivity, as the chlorophyll maximum occurs at 10 m, but concentration is low at 35 m (Figure 6, top). This is also supported by HoloCam data, which shows the presence of spherical droplets and/or gas bubbles with median diameter of approximately 40 µm between 30-35 m for MSN 3. The median opacity for these materials is 13 %. The HoloCam captured slightly higher numbers of spherical objects per image (max of 40), which is consistent with the higher scattering signal. Gulped samples were not collected at this location.

The second example is for oil detection in shallow waters where high FDOM and OBS optical signals were detected in waters southeast of the Campus Point area between 11-20 m during

MSN 7 suggesting the possible presence of petroleum oil (green and yellow symbols, Figure 7). Six gulped samples were collected – four between 11 – 13 m and two at 20 m. FDOM ranged between 2.75 - 3.17 ppb QSE and OBS values were 0.0010 – 0.0016 $m^{-1}sr^{-1}$ for these discrete samples. Vertical depth profiles show that the CHL maximum occurs between 5-10 m and is not coincident with elevated scattering and FDOM fluorescence. This suggests that the anomalies are not from biological activity below 11 m (Figure 6, bottom). The presence of oil was confirmed in the gulped samples, supporting the findings from the *in situ* optical sensors. BTEX and total alkane concentrations were elevated, ranging between 92.4 - 147.9 ng/L and 20 – 39.8 μg/L, respectively. Total PAH was also elevated, with highest concentrations, 5.3 and 4.2 μg/L for 12 and 20 m depth samples, respectively. It is important to note, that although oil was detected, the oil volumes in all the gulped samples are low in concentration with TPH values under 1.1 mg/L. Holographic images captured at the same time as gulped samples further offer support of the presence of oil (Figure 8). Images are processed through a routine to create a holograph where heatmap colors represent object distances from the detector with blue being farthest away at 160 mm and red being objects that are closest. Biological activity was detected by the imager, as illustrated by presence of copepods (yellow) and long chain plankton (green) in the left panel. The right panel illustrates a sample with minimal biological activity and the presence of oil spheres. The median sphere diameter measured by HoloCam was approximately 39 μm for all gulped samples during MSN 7 and a high number of spheres compared to other missions, as high as 154 per frame.

CONCLUSIONS

Oil spill monitoring efforts in remote locations such as the deep sea, offshore waters and under-ice environs is vastly improved by advances with *in situ* optical measurements from tethered and autonomous vehicles. Systems with suites of oil sensing tools (fluorescence, back scatter, holographic imaging, camera) allow for comprehensive three dimensional hydrocarbon mapping in dynamic environments. This is critical for response decision-making, providing rapid assessments of spilled oil at fine spatial and temporal resolutions during spill response operations or damage assessment activities.

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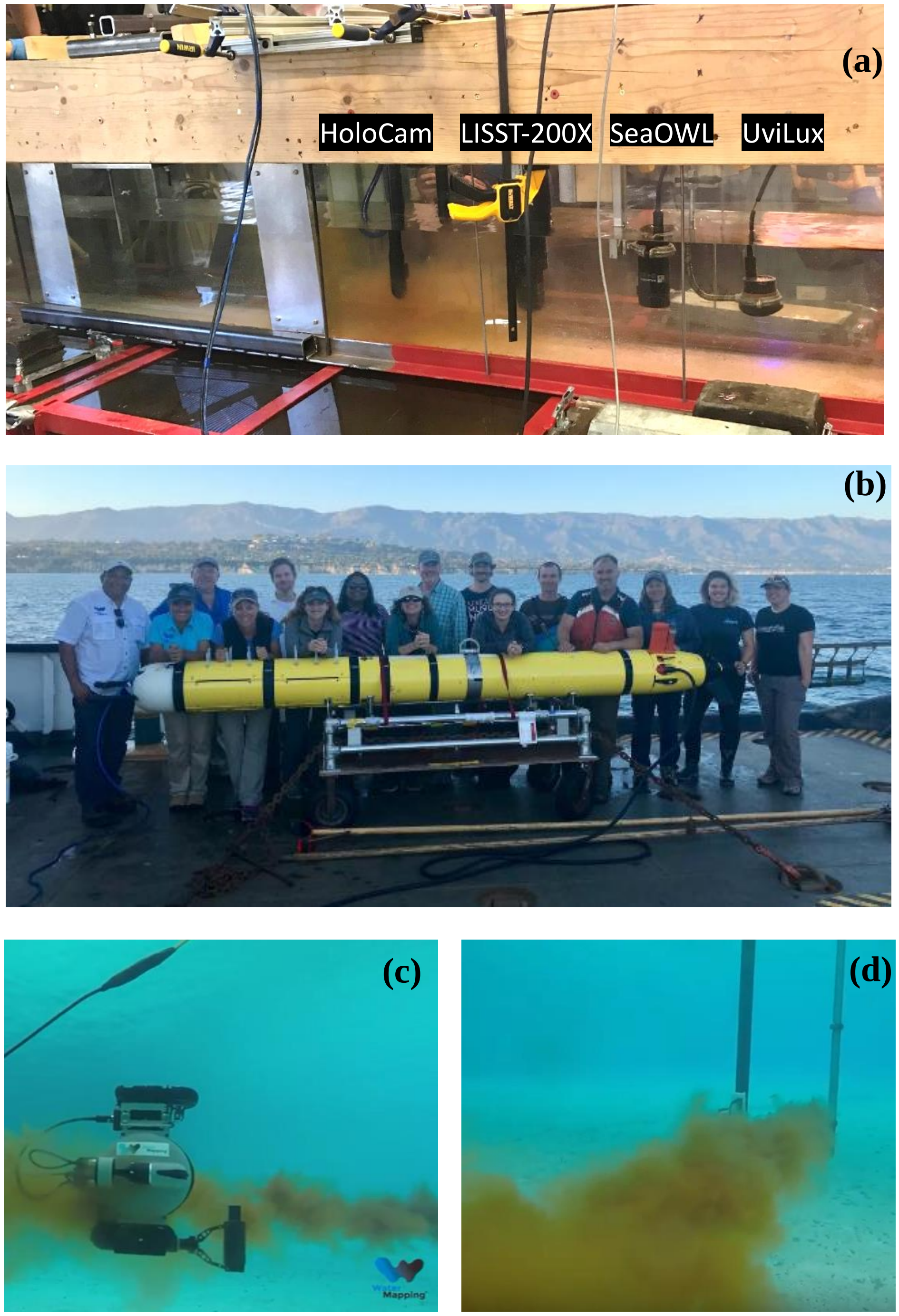


Figure 1. (a) Optical sensors mounted within CRRC flume tank during calibration, (b) REMUS-600 AUV aboard the USCGC George Cobb, and (c) Deep Trekker ROV in oil plume at Ohmsett wave tank and screen capture from the vehicle's video (d).

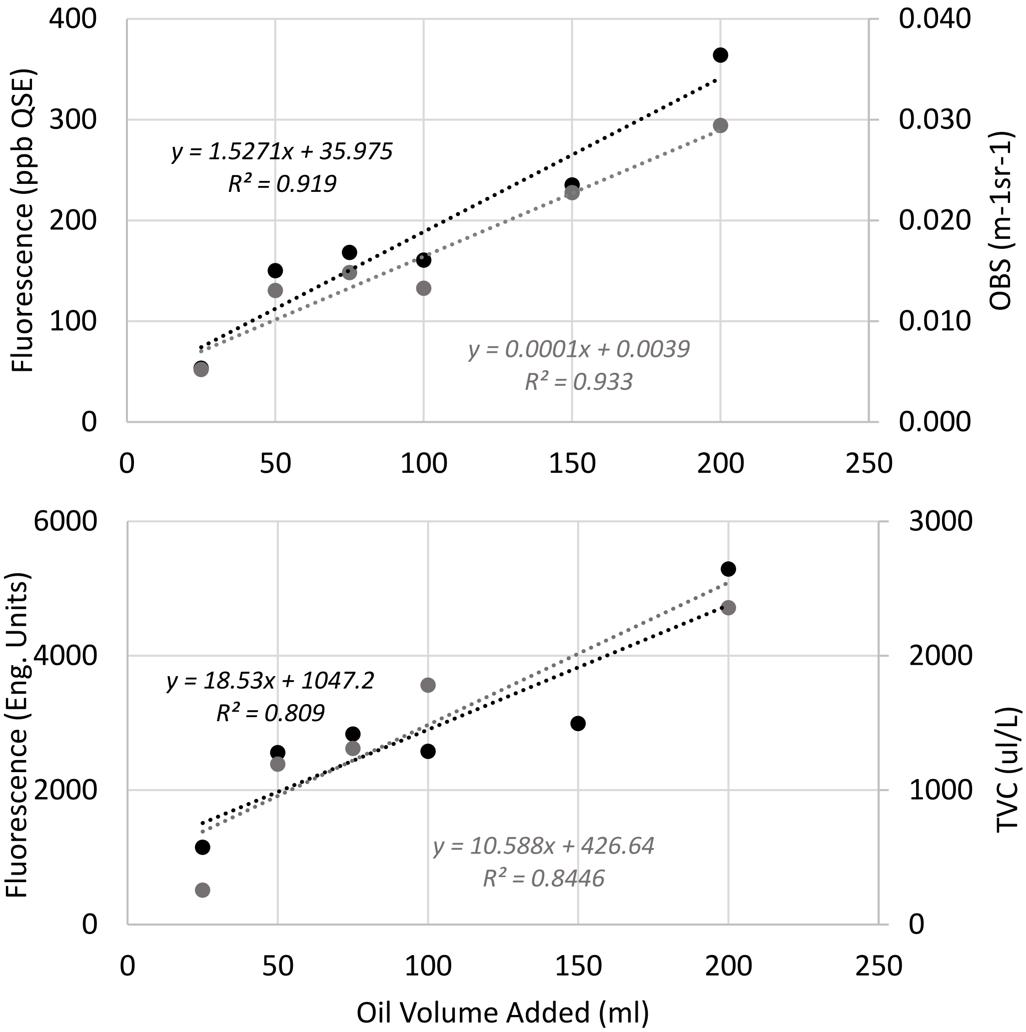


Figure 2. Linear response of SeaOWL UV-A fluorescence (black circles) and OBS (gray circles) linear response (top), and UviLux fluorescence (black) and LISST 200X Total Volume Concentration (gray) (bottom) to Hoops Crude Oil additions in the flume tank.

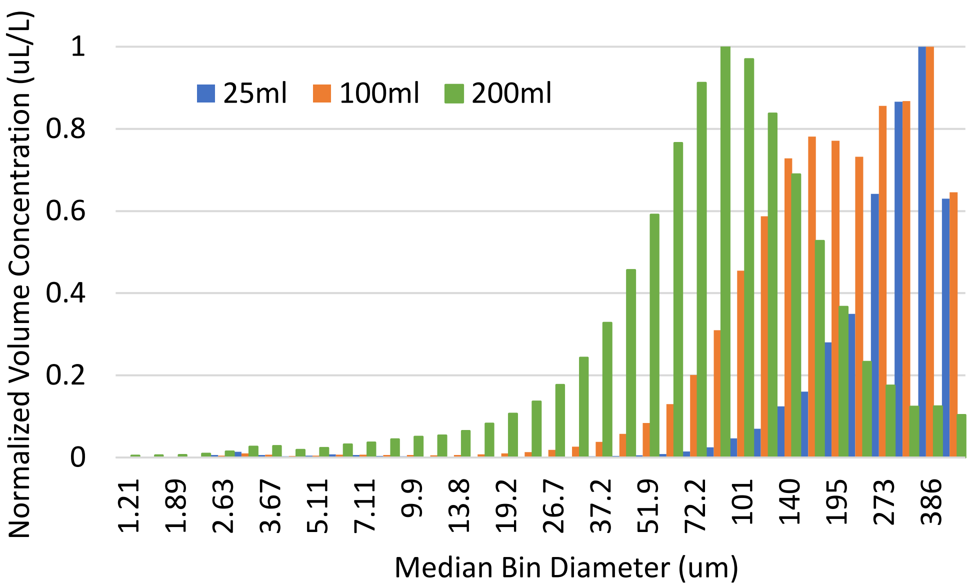


Figure 3. Oil Droplet Size Distribution for three volumes of Hoops Crude Oil added to the flume tank.

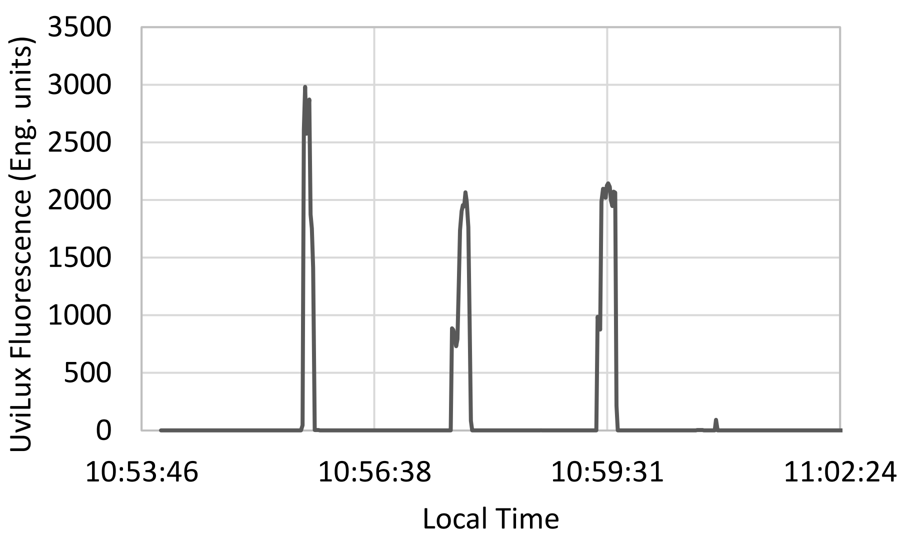
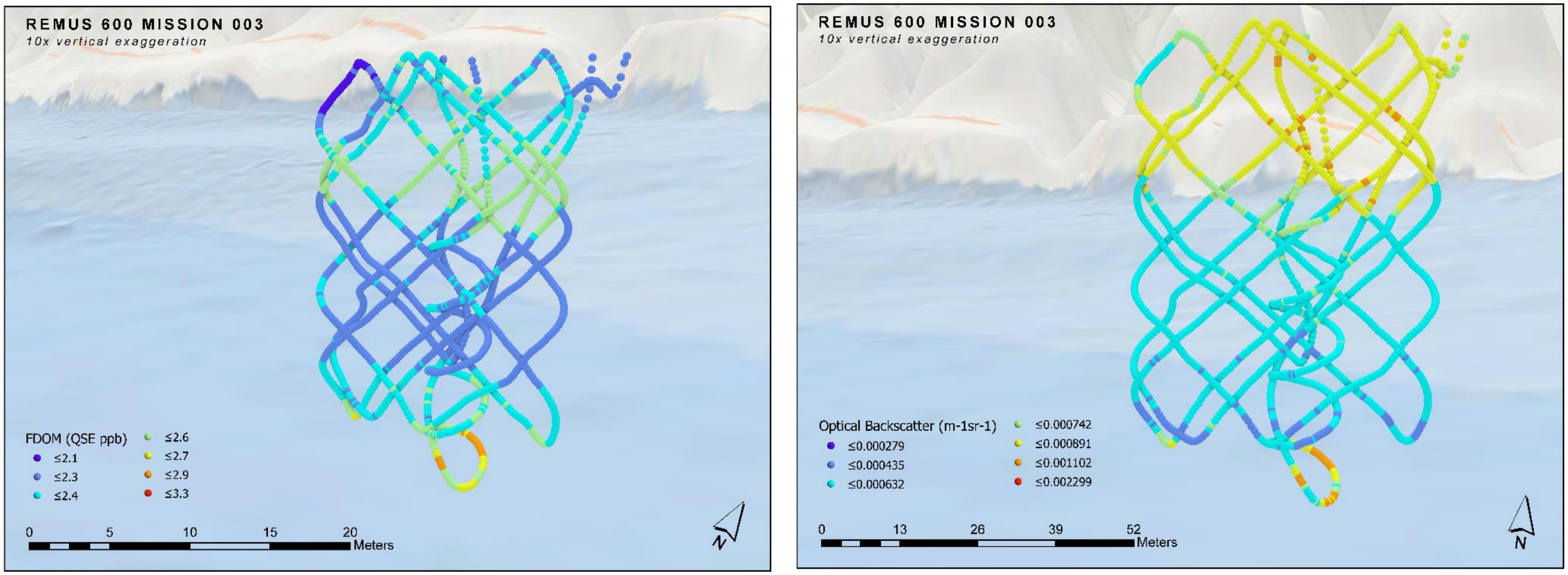


Figure 4. Time series of fluorescence intensity from the tethered ROV in the Ohmsett wave tank.



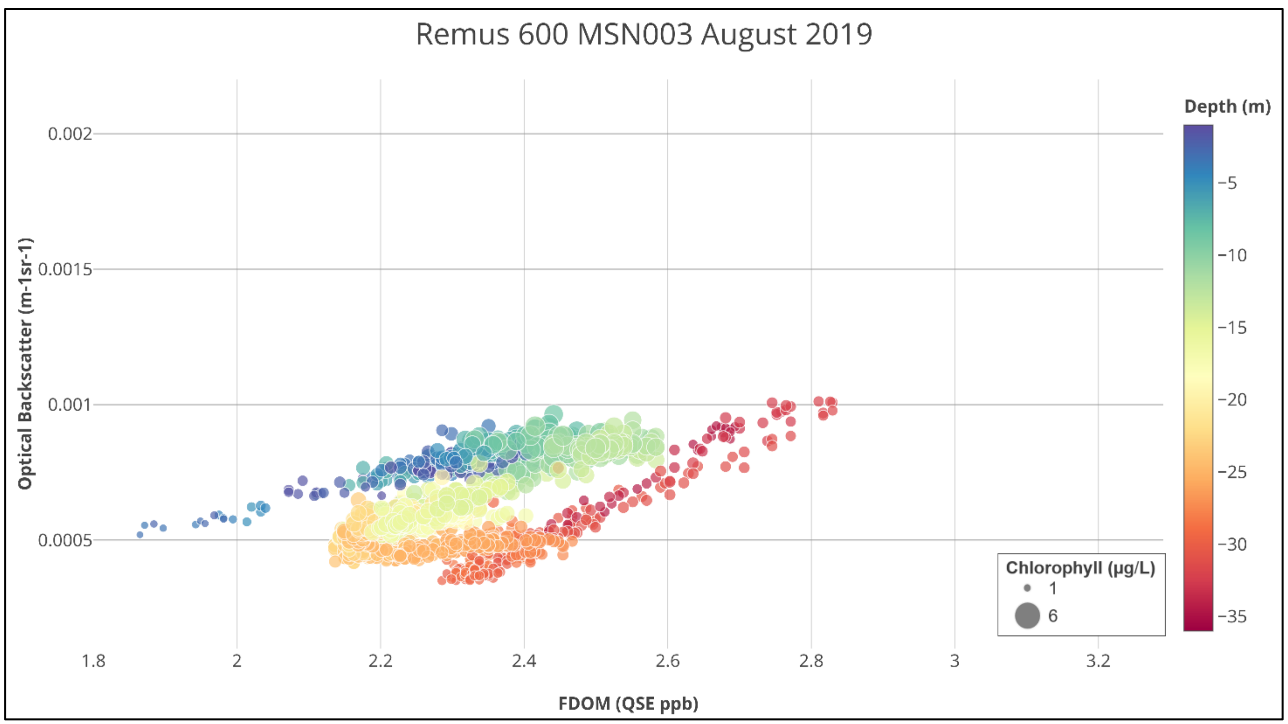


Figure 5. REMUS- 600 vehicle track (top) and scatter plot of optical backscatter as a function of FDOM (bottom) for Mission 3. Chlorophyll concentration is indicated by symbol size. Colors correspond to depth in the water column. High FDOM and OBS between 30-35 m (red circle symbols) suggests the presence of oil.

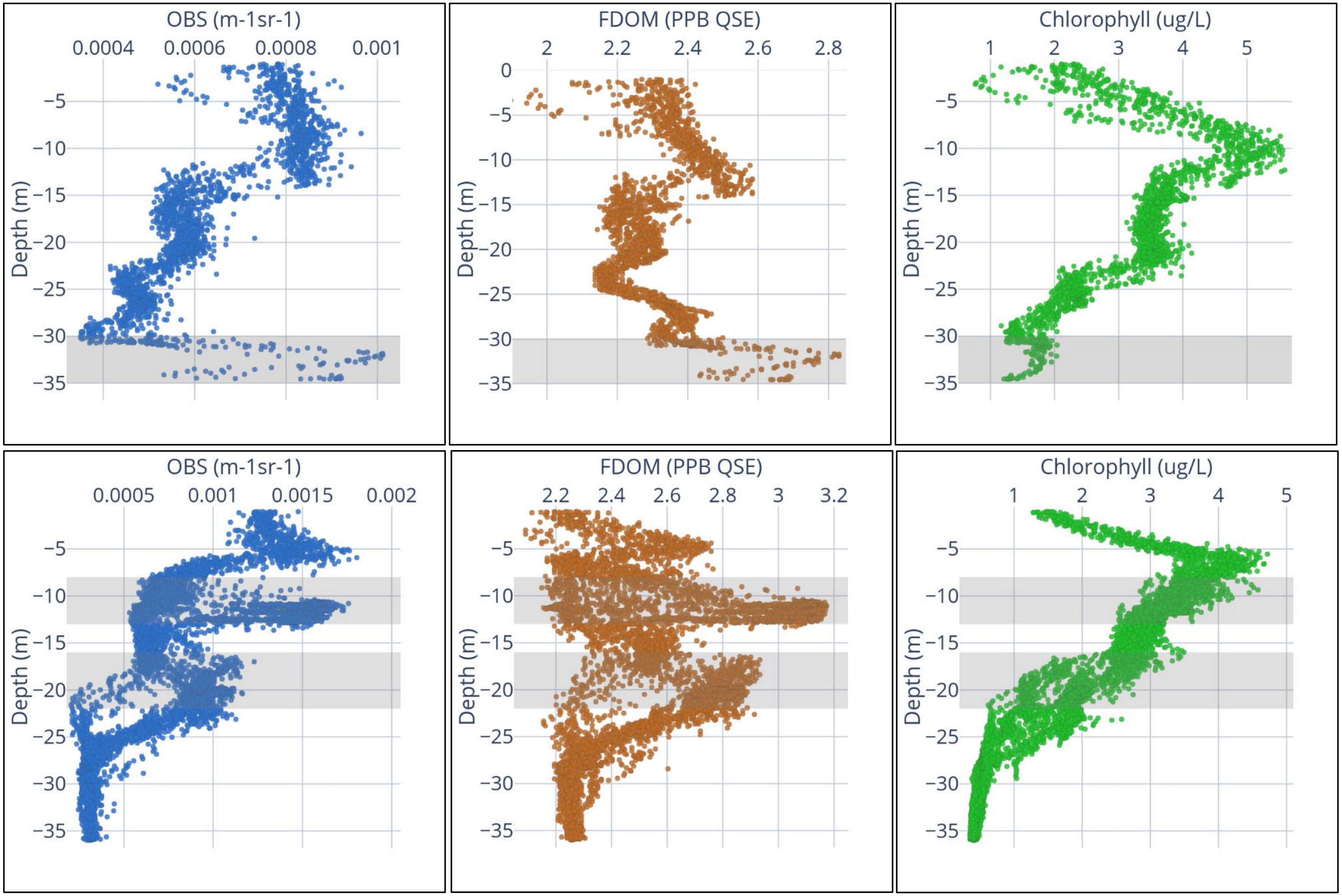
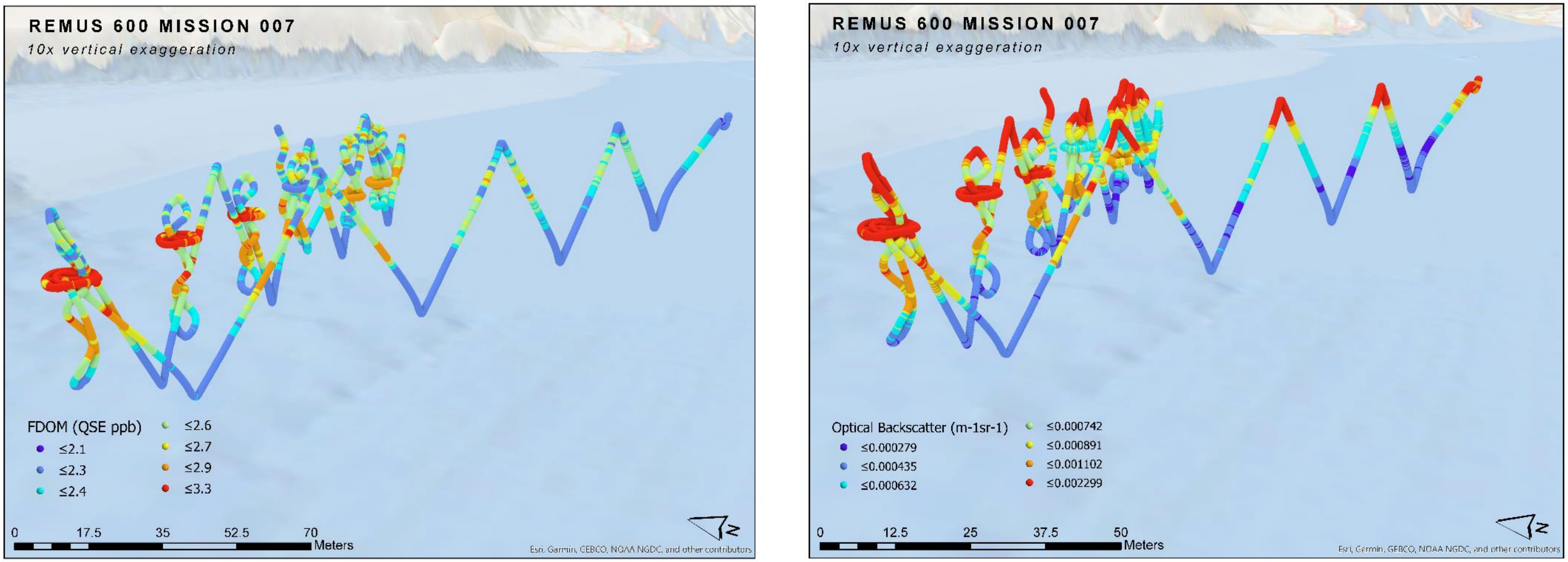


Figure 6. Depth vertical profiles of OBS (left), FDOM (middle) and CHL (right) near natural seeps. (top) During MSN 3 the CHL maximum is not coincident with elevated scattering and FDOM fluorescence, suggesting anomalies are not from biological activity at 35 m. (bottom) During MSN 7 the CHL maximum occurs between 5-10 m and is not coincident with elevated scattering and FDOM fluorescence, suggesting anomalies are not from biological activity below 10 m.



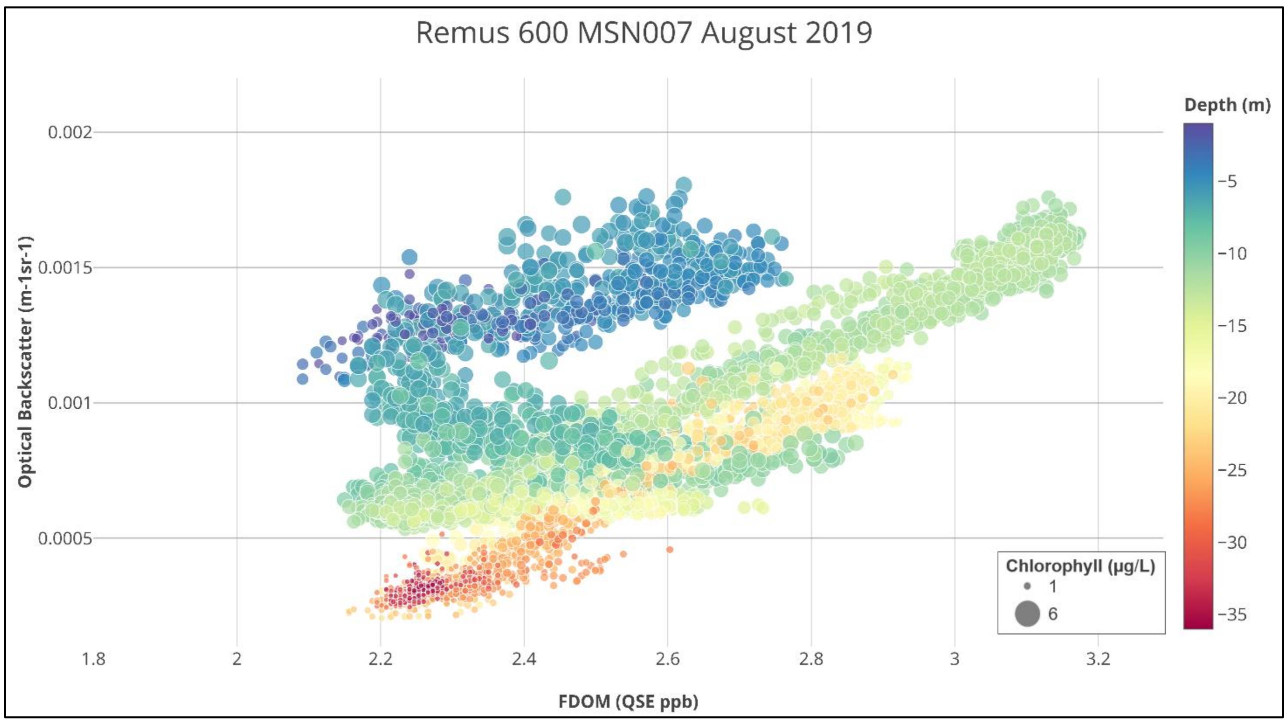


Figure 7. REMUS- 600 vehicle track (top) and scatter plot of optical backscatter as a function of FDOM (bottom) for Mission 7. Chlorophyll concentration is indicated by symbol size. Colors correspond to depth in the water column. High FDOM and OBS between 10-20 m suggests the presence of oil, confirmed by discrete samples of petroleum oil in water.

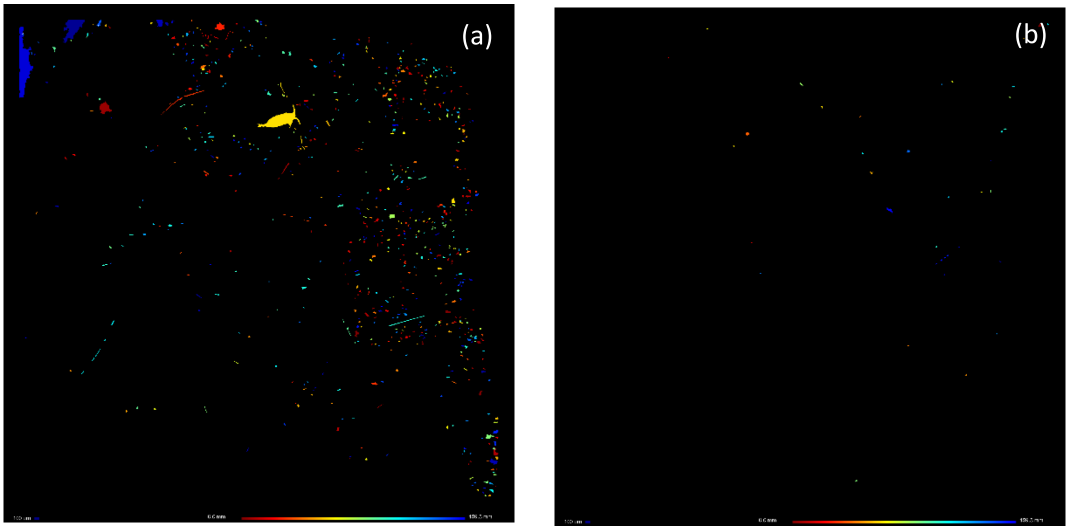


Figure 8. Image processing routine results for holographs collected during MSN 7 with the HoloCam. Heatmap colors in the holographs represent object distances from the detector with blue being farthest away at 160 mm. Panel a depicts biological activity detected by the imager, as illustrated by presence of copepods (yellow) and long chain plankton (green). Panel b illustrate a sample with minimal biological activity and the presence of oil spheres.