Deepwater Horizon Oil Spill NRDA Offshore Adaptive Sampling Strategies and Field Observations

James R. Payne, Ph.D.
Payne Environmental Consultants, Inc.
1991 Village Parkway, Suite 206B
Encinitas, CA 92024
760-613-7391 (cell)
jrpayne@sbcglobal.net

William B. Driskell
6536 20th Ave NE
Seattle, WA 98115
206-522-5930
bdriskell@comcast.net

August 2015

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Summary

Because of the subsurface release of Deepwater Horizon (DWH) oil from a depth of 1,500 m over an 87 day period, it was necessary to develop a number of adaptive sampling strategies to document the oil's fate and transport in the northern Gulf of Mexico over three dimensions and time. While oil continuously weathered as it was swept away from the wellhead by currents and winds, fresh oil within ~ 1.5-4 km of the source was surfacing every day.

When done properly, sampling the water column for hydrocarbons during or after an oil spill can be highly insightful, but the task is challenging with multiple opportunities for sample contamination without any feedback until weeks or months later when data come back from the lab. Sampling issues and solutions, and adaptive sampling strategies that proved highly effective for water and sediment sampling are presented. During the natural resource damage assessment (NRDA) cruises in the weeks and months after the Deepwater Horizon oil spill:

- Filtered, phase-separated water samples were collected in the field to later use in parsing out phase information (dissolved versus particulate) in the numerous unfiltered (whole water) samples collected.
- Adaptive sampling techniques were developed during early cruises to detect and sample within the deep plume rather than randomly or systematically collecting water samples at pre-assigned depths (a largely fruitless effort).
- Rosette samplers and later ROVs were equipped with real-time sensors (DO, fluorometry and CTD) to detect and sample the occurrence of oil at depth.
- ROVs were also equipped with video and cameras to visualize the oil and measure droplet size and concentration.
- During sediment collections, ROVs proved extremely valuable in sampling near-bottom water and identifying and collecting floc samples, burn residues, and sediments without disturbing the ephemeral oil layer at the sediment-water interface, and
- Field logistics and laboratory coordination efforts evolved allowing runner boats to pick up samples during extended offshore cruises, and during the year-and-a-half of sampling efforts after the Deepwater Horizon event, only 217 of 22,039 water samples (0.98%) were compromised by exceeding the AQAP 14-day maximum hold time.

Introduction

Water-column sampling for NRDA is perhaps the most technically demanding task of all oil-contaminated matrices. The primary difficulty is that unless the sample is being taken in close proximity to the source where oil is everywhere and suspended-droplets are still entrained in high concentrations (and likely visible), further afield, the oil and dissolved PAH concentrations are more typically found at ng/L (ppt) to µg/L (ppb) levels. At such trace concentrations, any sampling issue can easily become a confounded artifact, and on a vessel, there are multitudes of possible contamination sources to contend with. Furthermore, other than at the surface, any oil droplets in water will either be in motion and/or stratified at depth, which makes finding them difficult. Collected and analyzed properly, forensic water assessments are invaluable in directly confirming or modelling transport, mapping exposure, tracking fate, estimating toxicity, and quantifying injury, but the target is elusive and constantly changing its location and composition (Payne and Driskell, 2015a).

Given the circumstances, the scale and technical challenges of the Deepwater Horizon event (DWH), it should be no surprise that the sampling was not always executed perfectly, which suggests the resulting data should also be caveated. Some results are meaningful and highly insightful; others are confusing or confounded with errors or were simply misguided in collection. This document reports the context of the offshore water sampling and the evolving efforts developed to track the deep plume. Initial efforts were certainly less focused and underequipped for the task, e.g., some cruises collected water at pre-assigned depths (expecting oil would form a uniform gradient in the water column?). Through a steep learning curve, instrument and logistical solutions were conceived and deployed in the field to make the observations and collect the samples needed to understand and document the event to meet NRDA needs despite the impediments of weather, technical and logistic challenges, constraints from response operations, and navigating the bureaucratic/social/political fog of war(-like) ambiance.

Phase Sampling

Knowing from past spills that understanding and modeling the fate and transport behavior of the waterborne oil would require documenting both dissolved and particulate oil phases (for reasons described below), the DWH Water Column Technical Working Group (TWG) made it a priority to obtain a comprehensive set of field-filtered water samples. The filtered data would later become the reference series of weathered particulate oils used in fingerprinting and to report phase-discriminated data for water-column modelling (Payne and Driskell, 2015b).

Driven by dissolution/weathering processes, oil is present in water in both dissolved and particulate (oil-droplet) phases, which, for PAH molecules, correlate with their diverse, yet mostly predictable, wide range of individual water solubilities (McAuliffe, 1963, 1966, 1977a,b, 1987; Payne et al., 1984, 1991a,b, 2005; Payne and McNabb, Jr. 1984; Payne and Phillips, 1985; NRC, 1985, 1989, 2003, 2005; Wolfe et al., 1994; Payne and Driskell, 2003). For example, in the DWH water-column, it was expected that the highly soluble BTEX components would occur primarily in the dissolved phase (Camilli et al., 2010; Reddy et al., 2011) derived either from the jetted gases or stripped from oil droplets during their ascent to the surface. In contrast, the insoluble higher-molecular-weight (HMW) n-alkanes (C_{12}-C_{40}), hopane, and other biomarkers exist almost exclusively in the oil phase or as very fine colloidal fractions in dissolved-

phase samples. While general dissolution patterns of DWH oil were as expected, the exact partitioning behavior of oil within the entrained deep plume and the larger oil droplets rising through the water column and advecting away from the source were not as well understood (Socolofsky et al., 2011).

To fill this knowledge gap, water-column samples were processed at time of collection with the Portable Large Volume Water Sampling System (PLVWSS) developed by Payne, et al. (1999) to allow examination of separate dissolved- and particulate/oil-phases on three *Jack Fitz* cruises (May-June 2010), the first *American Diver* cruise (August 2010), four *HOS Davis* cruises (August – December 2010), and in 2011, on five individual *HOS Sweet Water* cruise legs (March/April, July/August, and October/November 2011). Immediately after securing the collection bottles on deck, two 40 mL aliquots for VOA analysis were removed from the bottom sampling valve of the collection bottles, and then separate 1 L bottles were drained for Entrix/BP sample splits and NOAA duplicates if desired. These splits also included samples for total suspended solids (TSD), dispersants, and toxicity if requested. Following this initial aliquot removal, ~3.5 L from the remaining volume in the sample bottle was vacuum filtered through the PLVWSS for separation of the particulate/oil and dissolved phases (Figure 1). The particulate/oil phase trapped on the 0.7 µm glass fiber filter (Figure 2) was stored frozen, and the dissolved phase in the 3.8 L amber glass jug housed in the PLVWSS pump box was left in the jug and refrigerated at 2° C. The PLVWSS was designed to use 3.8 L, I-CHEM certified-clean amber glass jugs that were secured in the (oil-less) vacuum pump box to minimize possible breakage from otherwise being placed loose on deck, and the protocol allowed sample processing with minimum exposure to exhaust fumes and other potential ship-board contaminants (Payne et al., 1999).

Figure 1. Vacuum filtration of dissolved and particulate fractions from a 5 L GoFlo bottle secured on deck soon after collection. The transfer tubing from the bottom sampling valve on the bottle allows the water to first pass through a 0.7 µm glass fiber filter housed in the stainless steel filtration unit (on top of second box) and then into the amber-glass jug in the vacuum pump box (foreground).

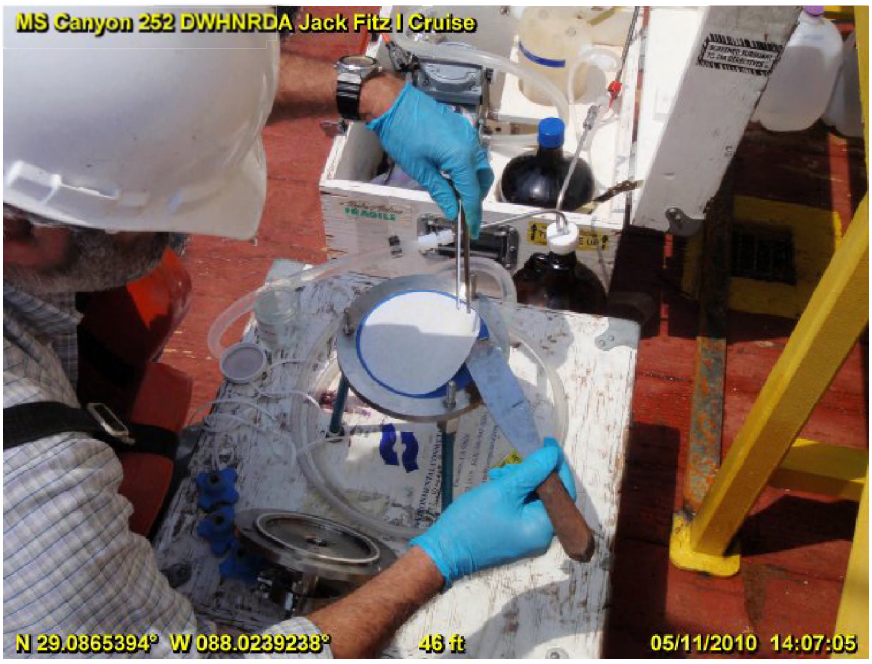


Figure 2. After collection, the 142 mm diameter filter containing the particulate oil phase is carefully removed from the filter housing and frozen in a 125 mL sample jar. The dissolved phase contained in the 3.8 L I-CHEM certified-clean amber glass jug (still in the vacuum-pump box – blue cap) was refrigerated at 2° C.

Filter and filtrate (particulate and dissolved) data from a fresh sample collected at depth near the wellhead (Figure 3) illustrate the enrichment of low- and mid-molecular-weight (LMW and MMW) parent and alkylated PAH in the dissolved phase with concomitant depletion of these same components in the particulate oil phase trapped on the filter (left-hand column). Likewise, the insoluble high molecular weight (HMW) (> C_{12}) n-alkanes and isoprenoids (i.e., saturated hydrocarbons – SHC) are almost exclusively found in the particulate/oil phase trapped on the filter (upper right-hand plot) with just traces of colloidal material that presumably broke through the filter and into the dissolved phase (lower right-hand plot) (note the scale differences when comparing the particulate and dissolved phase SHC plots, and that the apparently elevated dissolved-phase C_{18}, C_{25}, and C_{28} are lab artifacts only showing up in extremely low-concentration samples). Absence of LMW components in the particulate phase indicates that significant dissolution weathering for both aromatics and < C_{12} aliphatics occurred while the oil was still at depth and very close to the wellhead.

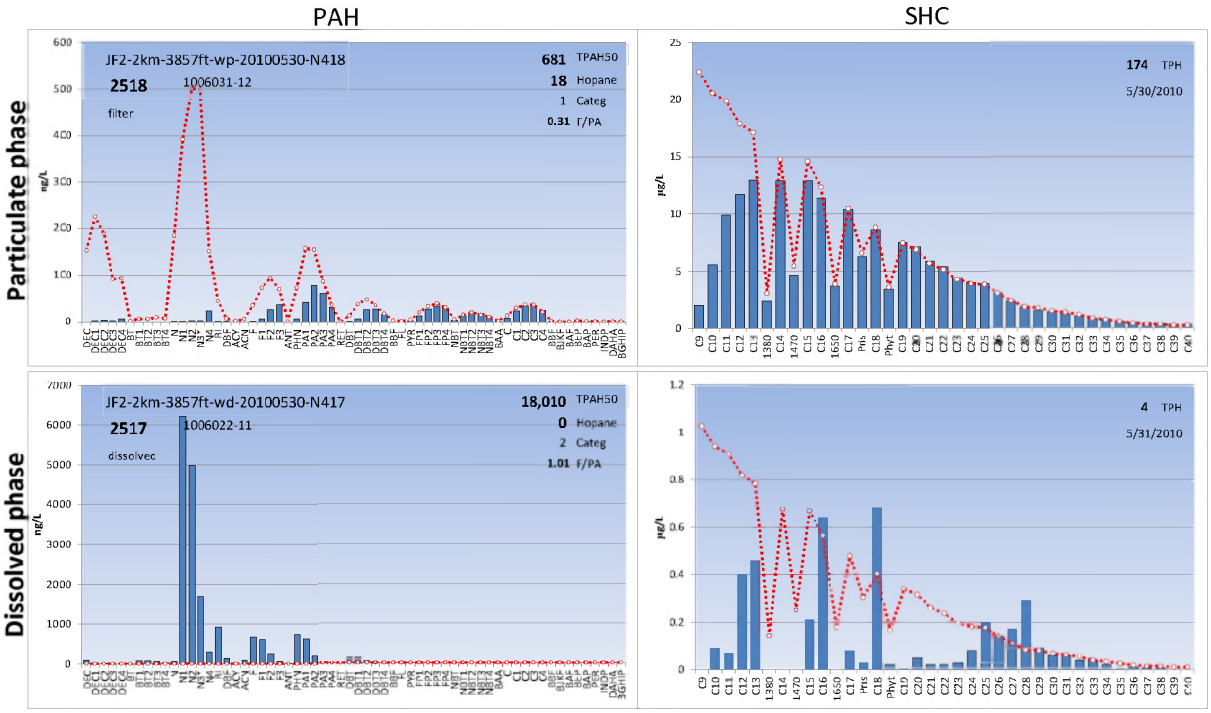


Figure 3. Paired filtered particulate/oil- and dissolved-phase PAH and n-alkane (SHC) profiles from 1,176 m, 2.0 km SW of the wellhead, 30 May 2010. Reference PAH (red) is fresh DWH oil normalized to C2-naphthobenzothiophene (NBT2) showing enhanced dissolution of lower-molecular-weight PAH in the dissolved phase (lower plots) and depletion of these same constituents in the particulate/oil-phase (upper plots). Higher-molecular-weight SHC (normalized to n-C26 in fresh MC252 oil) occur primarily in the particulate phase (upper right – note the differences in concentration and scale vs. the dissolved phase – lower right) with selective dissolution of C_9-C_{13} range particulate components with little or no changes for alkanes and isoprenoids above C_{14}.

Filtering samples at the time of collection requires extra time and attention to process and later analysis. Thus, the goal was not to filter all samples but merely sufficient numbers to document and understand the DWH phase-partitioning behavior. Later, during forensic assessments, the filter components were compiled as a series of weathered particulate-phase samples and used for parsing out phase assignments in unfiltered samples (described in Payne and Driskell 2015b). These phase data were provided to modelers along with the forensic calls to compare water exposure model outputs to sampling results as a means of evaluating the modeling.

Assuming hopane as a conservative tracer, based on TPAH/hopane-depletion calculations, the freshest oil found in the NRDA water samples (at 758 m on 30 June 2010, 2 km and 214° from the wellhead) was already ~47% TPAH depleted (primarily dissolution of naphthalenes). Other samples collected at this station at 304 and 21 m showed continued dissolution weathering with 74 and 81% depletion, respectively, as the larger droplets rose to the surface. Although these data appear as a gradient, it is not possible to estimate dissolution kinetics or rising velocities from oil droplets in grab water samples. The droplets are not just passing straight up through the water column; water masses are moving back and forth from different directions as suggested by Valentine et al. (2011) and ADCP current data. Hence, at each depth, an oiled-water sample could represent a mixture with any entrained residual oil.

Adaptive Sampling

For the Deepwater Horizon event, the challenges of tracking and sampling an extended plume of oil-contaminated water between ~1,000 and 1,300 m was met with some innovative adaptive sampling methods. From remotely operated vehicle (ROV) teams monitoring the wellhead (on the *Skansi Neptune*, Driskell personal observation, 2010), it was known that a major oil plume was forming at ~1000 m depth above the wellhead with some additional stratification higher in the water column. During several early cruises, shipboard observations along with satellite and aircraft overflights documented the location of the surfacing oil, which generally was used to help identify stations of interest, but using Acoustic Doppler Current Profiler (ADCP) data, modelers from RPS Applied Science Associates (ASA) were successful in predicting subsurface oil transport separate from surface oil and then redirecting sampling efforts. On 30 May 2010, surface oil was observed in extensive coverage to the north of the wellhead, but using ADCP data and modelled plume dynamics, ASA directed the *Jack Fitz* efforts out of the surface oil to a station 2.2 km SSW of the wellhead in search of the subsurface plume. Very little surface oil was observed at that station, and no oil was encountered with the real-time instrumentation on the ROV (Figure 4 and Figure 5) until the sampling platform reached 1082 m. At that depth, for the first time on NOAA-directed NRDA cruises, the subsurface plume was documented advecting away from the wellhead without the surface manifestation of freshly rising oil. This was the first evidence we had that the surface slick and deep plume were not necessarily coupled (discussed further below).

During the early stages of the spill, a few cruises non-productively attempted to sample water at fixed, predetermined stations and depths. Many of these water samples came back as non-detects because, in general, oil does not form in a depth gradient and the samplers missed the submerged plume. More insightful sampling brought CTD, dissolved oxygen (DO) and fluorometry instruments to find submerged concentrations of oil prior to sampling. This scheme was successful in finding the oil but the lag between making the instrument drop, locating oil, retrieving the instruments and deploying a rosette to the recorded depths meant the desired water mass containing the oil may or may not be relocated during the subsequent blind drop. It was then obvious that the instruments and sample bottles should be combined on the same deployment package and use live sensor returns. The usual procedure was to use the sensors, primarily dissolved oxygen and fluorometry, to locate target sampling depths on the downcast and while at the bottom of the cast, decide the target sampling depths for the available bottles. Then on the upcast (retrieval), reconfirm the sensor indications, and collect the samples. To best define the plume, bracketed samples would be taken ~50-100 m below, at the center of, and ~50-100 m above the target depths.

On other cruises, the scheme was further advanced using ROVs and enhanced sensor packages to better inform real-time sampling decisions.

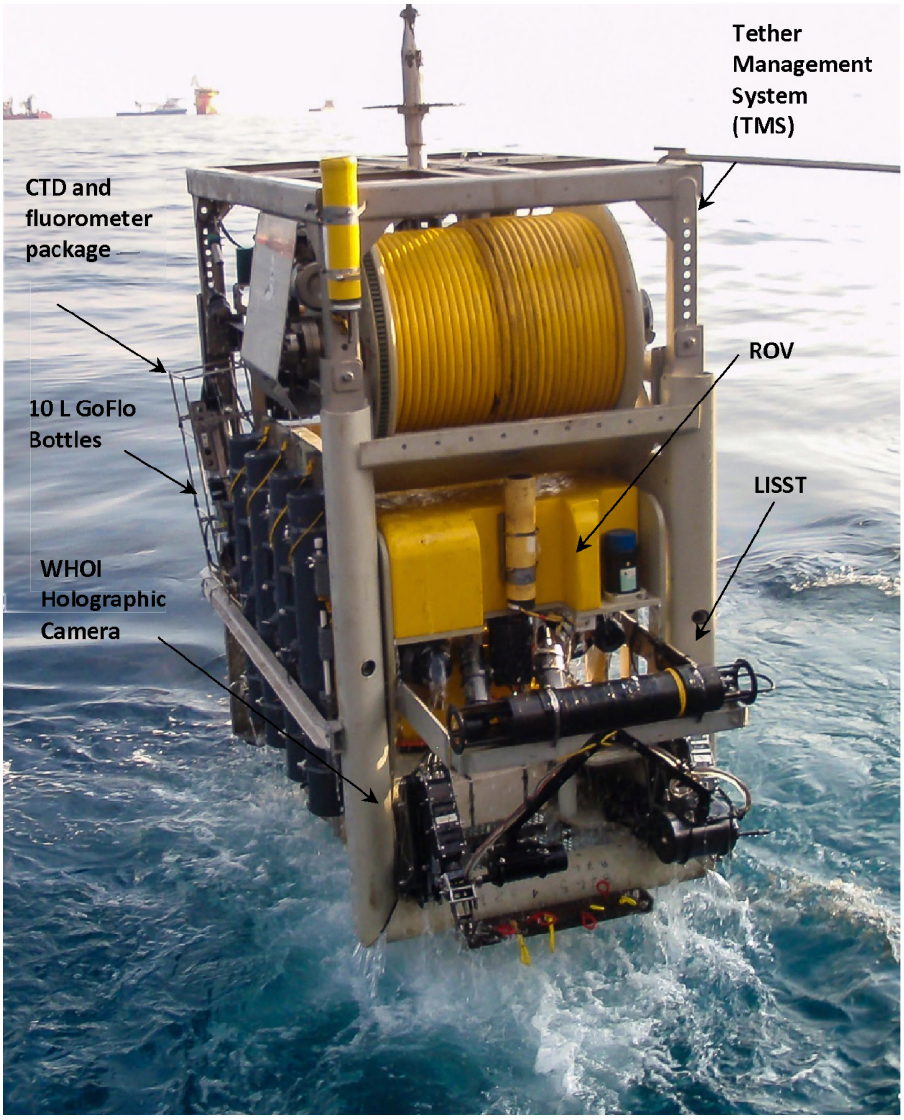


Figure 4. Remotely Operated Vehicle (ROV) equipped with CTD package for temp, salinity, dissolved oxygen, and pH, fluorometers for in situ oil/PAH measurements, 670 kHz and 300 kHz forward-looking sonar systems (internal to the ROV), 10 L GoFlo bottles, video camera with visible and UV/black-light, Laser In Situ Scattering and Transmissometry (LISST) instrument, and WHOI holographic camera for recording oil-droplet-size distributions.

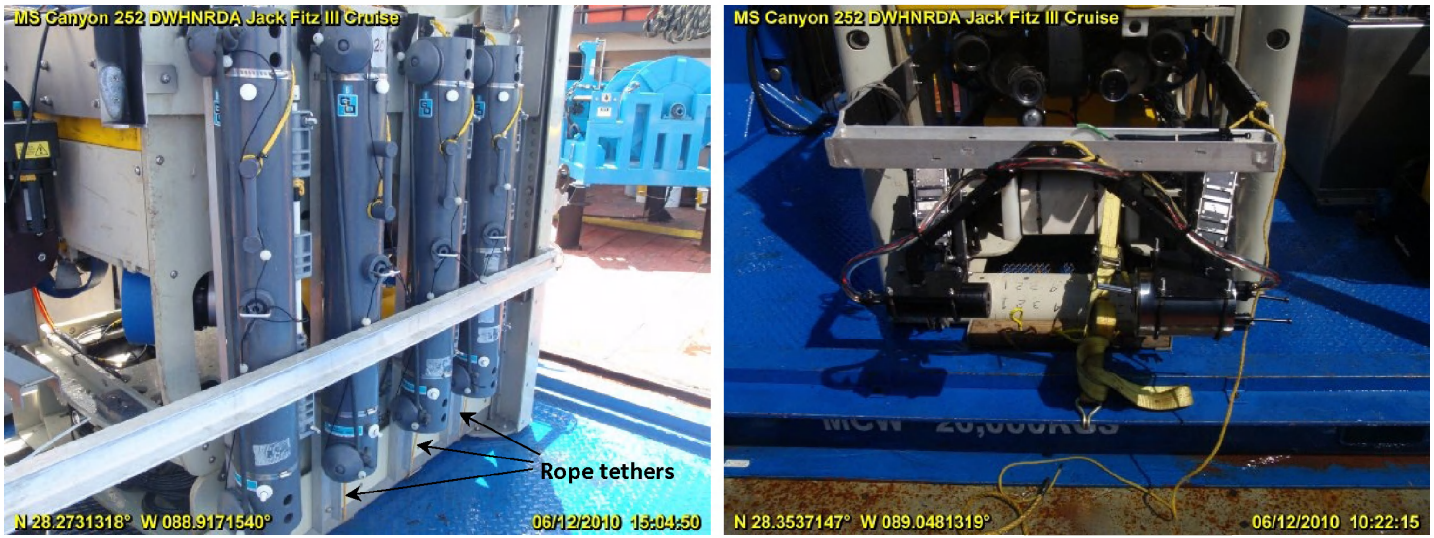


Figure 5. Remotely Operated Vehicle (ROV) on the *Jack Fitz* equipped with 10 L Go-Flo Bottles (left) and a Holographic Camera and Video Camera with Tungsten (Visible) and UV (Black) Lights (right). The yellow tethers attached to each GoFlo bottle allowed them to be tripped without having to "fly" the ROV out of the TMS cage.

Finding and Tracking the Subsurface Oil Plume

During *Jack Fitz* cruises in May and June 2010, an ROV was equipped to allow real-time video observations of sub-surface plumes and simultaneous measurements of CTD, DO, turbidity, and fluorescence data to better inform water column sampling decisions and allow synoptic sampling with other sensors (Figure 4 and Figure 5). After several iterations, the ROV was optimally configured with the following instrument packages:

- CTD package for temp, salinity, dissolved oxygen, and pH with depth
- Fluorometers for oil/PAH measurements
- 670 kHz and 300 kHz forward-looking sonar systems (standard ROV packages)
- 5, 10, or 20 L Go-Flo Bottles
- Video Camera with tungsten (visible) and UV/black lights
- Woods Hole Oceanographic Institution (WHOI) Holographic Camera (provided and operated by Dr. Cabell Davis and Nick Lomas, WHOI)
- LISST for oil droplet size determinations (only to 250-300 m)

During early ROV excursions near the wellhead, oil-droplet concentrations were still high enough that it was possible to detect subsurface oil lenses in live video images. At a single location, the distinct, vertical oil distribution was visible in images taken at different depths (Figure 6). In clear water, the ROV's hydraulic arm and a horizontally-mounted GoFlo Bottle were easily visible with the video camera but as the ROV entered a subsurface oil lens, the images became obscured as if looking through a brown "oil fog." When viewed with the UV/black light, larger oil droplets fluoresced brightly, appearing as streaks in the images (due to the surface-vessel-induced pitching motion of the ROV still secured in the Tether Management System (TMS)). This visual approach, combined with watching for oil-droplet accumulations on a 4 x 4 cm^2 oil droplet-quantitation grid mounted on the underside of the ROV's ceiling plate (Figure 7), both confirmed other sensor readings and established an observational model for finding the oil and better estimating droplet size distributions (Li et al. 2015). The visual confirmation was invaluable on the *Jack Fitz* 2 and 3 cruises because, at that time, the available fluorometer, a Turner Self-Contained Underwater Fluorescence Apparatus® (SCUFA) was the only available model for that vessel. The SCUFA was designed with 460 nm excitation and 685 nm emission wavelengths and while good for other research purposes, these wavelengths were not optimal for producing a reliable oil fluorescence signal.

By mid-June on the *Jack Fitz* 3 cruise, a turbidity signal along with significant DO sags were being used to delineate subsurface plumes in real time. Photographs of the live CTD/turbidity/DO traces obtained during the dives (Figure 8 and Figure 9) demonstrate the data available to assist in sample-depth selections. The turbidity (blue trace) showed spikes and trends that corresponded to DO sags, which suggested the presence of oil droplets. Success was achieved on cruises with different fluorometer packages including Colored Dissolved Organic Material® (CDOM) instruments with 370 nm excitation and 460 nm emission wavelengths on the *Brooks-McCall*, *Ocean Veritas*, *Thomas Jefferson*, and several Response Cruises. Note that wavelengths are mentioned as a caveat relevant to evaluating

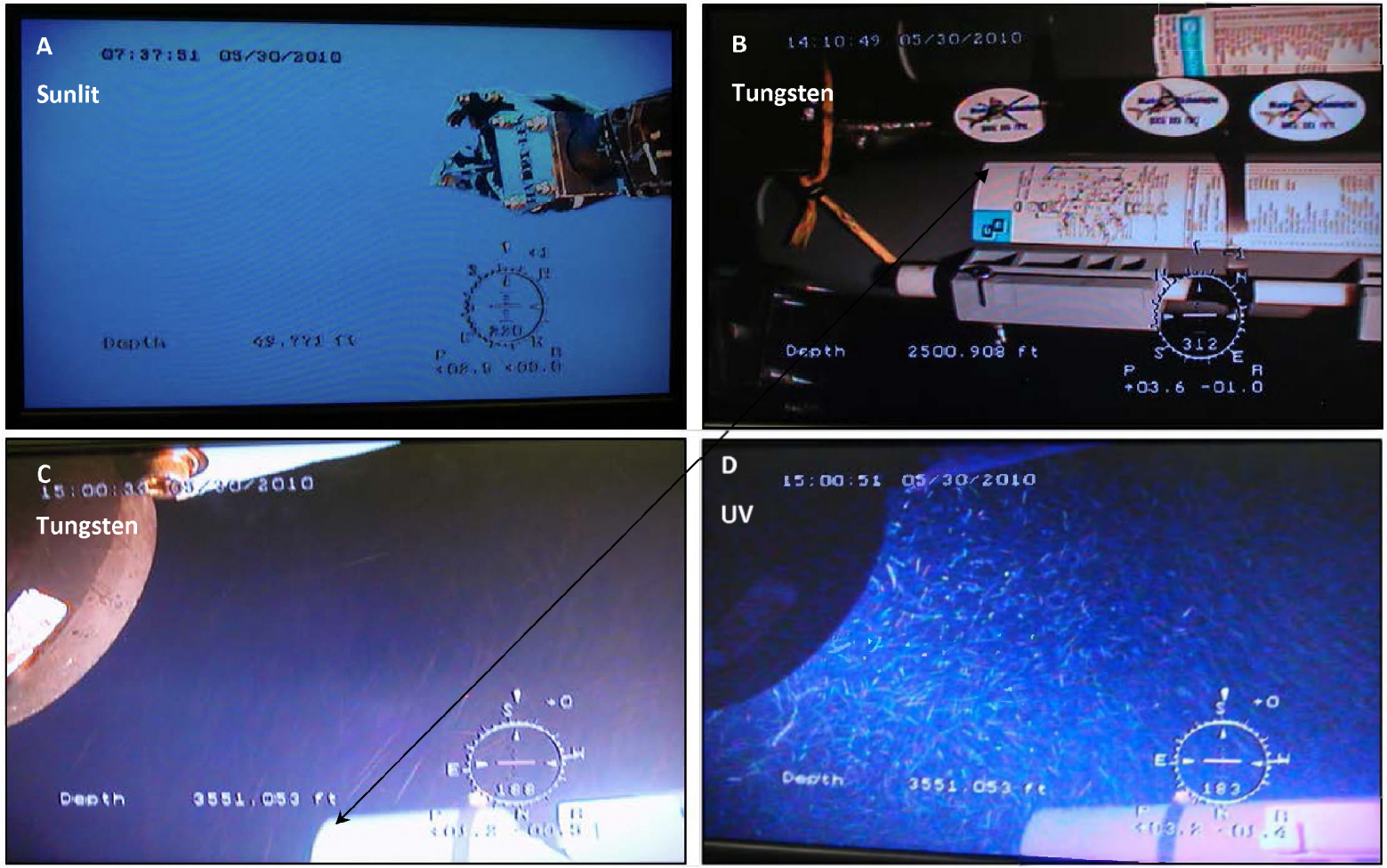


Figure 6. ROV video screen grabs of A) the ROV hydraulic arm approximately 0.6 m (2 ft) in front of the video camera at 15 m (50 ft) in clean water illuminated with natural sunlight from the surface; B) horizontally mounted GoFlo Bottle in front of the ROV at 762 m (2501 ft) in clean water illuminated with tungsten (white) light; C) the horizontally mounted GoFlo Bottle in front of the ROV at 1,083 m (3,551 ft) in a subsurface oil plume illuminated with tungsten (white) light; and D) the horizontally mounted GoFlo Bottle in front of the ROV at 1,083 m (3,551 ft) in a subsurface oil plume illuminated with black light. All photographs obtained at the same station location as Figure 7.

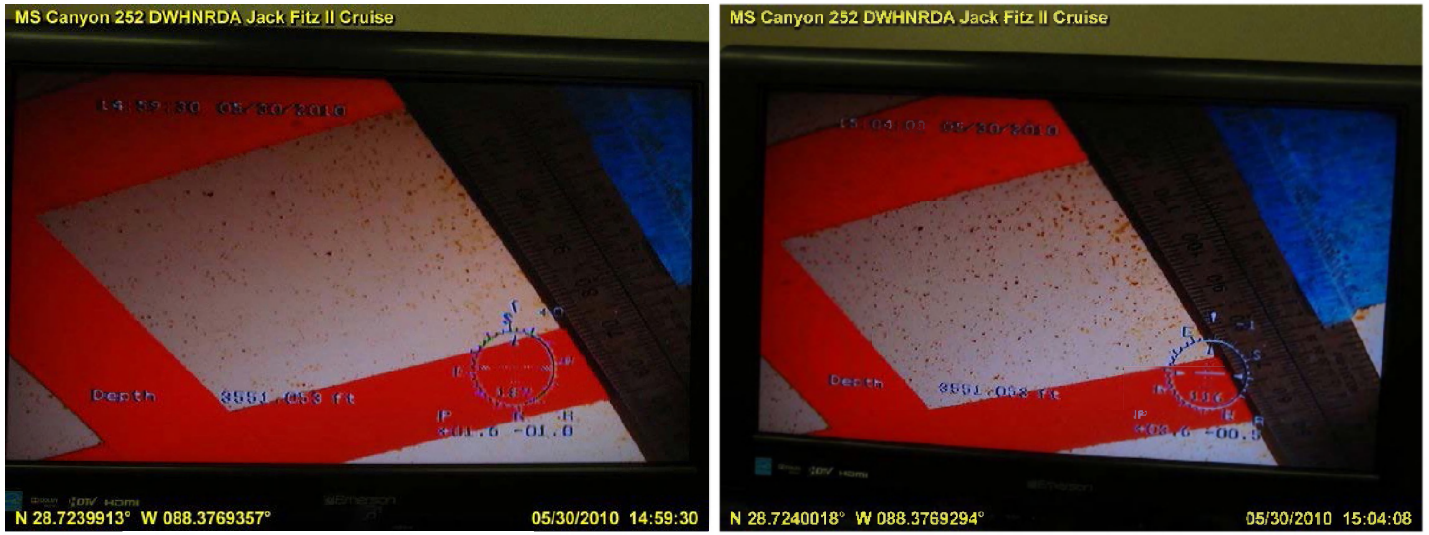


Figure 7. Screen-grabs of 4 x 4 cm^2 oil quantitation grid mounted on the underside of the ROV ceiling allowing time-lapse and video photography of finite oil droplets accumulating at specific depths. These photographs show the oil droplets accumulating over a 5 minute interval while holding station at a depth of 1,083 m (3,551 ft) at station JF2-2k-053010, 2.2 km and 214 degrees (SSW) from the wellhead on 05/30/10.

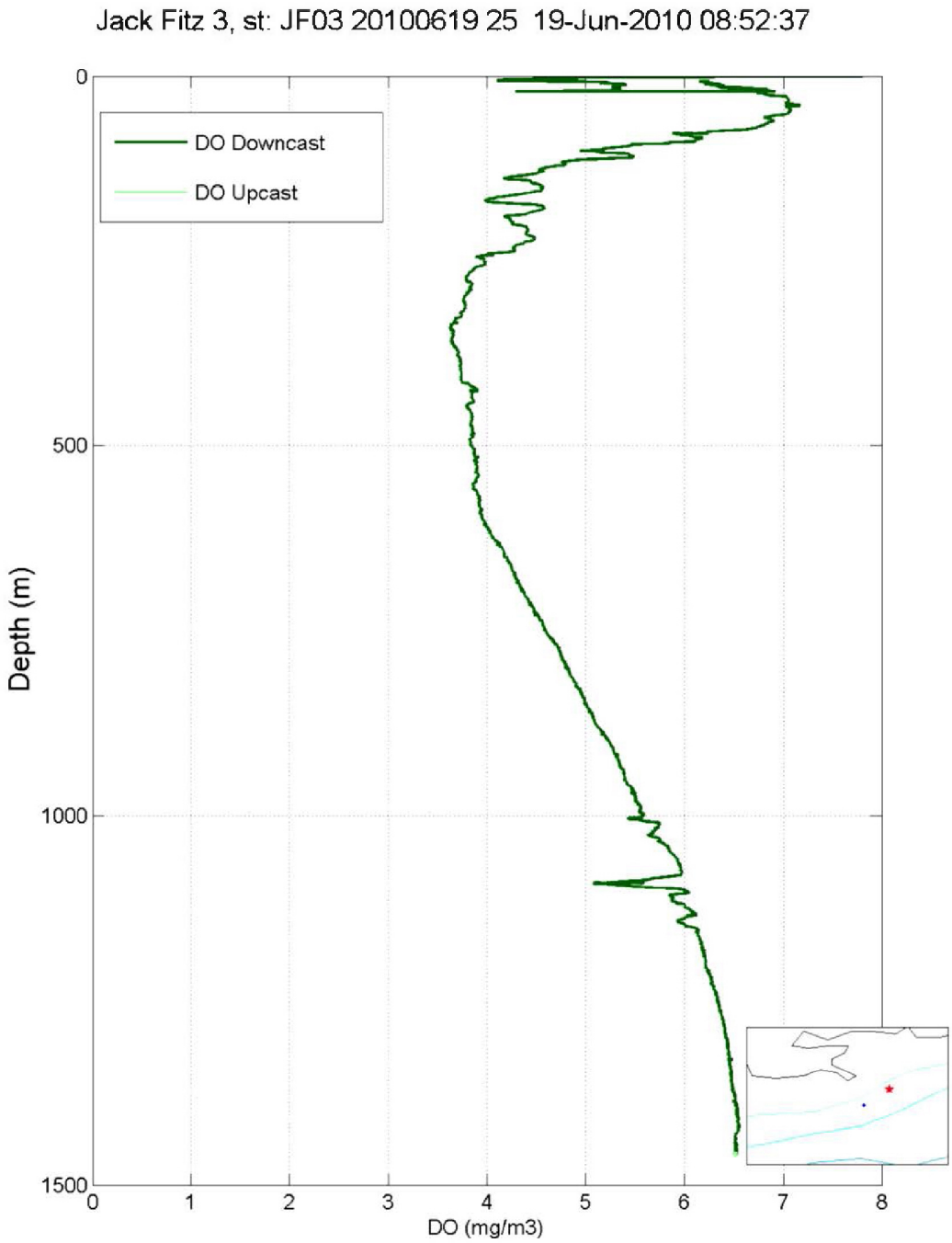


Figure 8. Dissolved oxygen (DO) profile from a 19 June 2010 *Jack Fitz* 3 ROV dive showing near surface (100-250 m) DO anomalies and a sharp DO sag at 1100 m, with smaller DO sags at 1020, 1120, and 1180 m. A photograph of the corresponding real time CTD/DO/ turbidity profile obtained during the dive is shown in Figure 9.

Figure 9. Photograph of the real-time CTD/DO/turbidity profile obtained during a 19 June 2010 *Jack Fitz* 3 ROV dive showing the temperature (red), DO (green), salinity (yellow) and turbidity (blue) data with depth. There is a correspondence between the DO sags with the turbidity profile, but unfortunately, no fluorometry data were available. See corresponding digital DO profile in Figure 8.

fluorometry (particularly SCUFA) data collected in earlier NRDA efforts. It was only later when Chelsea AquaTracka® fluorometers, tuned for oil detection with 239 nm excitation and 360 nm emission wavelengths, were used on the *American Diver*, *HOS Davis*, and *HOS Sweet Water* cruises that more reliable *in situ* fluorometry data were obtained. But even these wavelengths are generally selected for detecting *refined* petroleum products; Chelsea makes a 239/440 nm model optimized for crude oil, but they were not available at the time. During forensic analysis, these fluorometry and DO data were instrumental in confirming subsurface plume samples when the PAH and SHC signals were significantly degraded or diluted. On cruises lacking reliable fluorometry data, the ability to confidently match profiles to MC252 suffers due to the lack of secondary confirming evidence (see forensic fingerprinting methods tech report, Payne & Driskell, 2015b). Across-platform data comparability was optimal when vessels were equipped with similar instrument packages comprising CTD, DO, and Chelsea AquaTracka fluorometers specifically designed for oil detection (239 nm excitation and 360 nm emission wavelengths). For example, in a calibration check, AquaTracka and DO data collected from Station T6S3 by the *NOAA vessel Pisces* on 1 September 2010 approximately 2-3 hours prior to being re-sampled by the *HOS Davis* showed very similar DO and fluorometry signals (even down to the fine plume structure; Figure 10). These results also demonstrated the continuity and homogeneity of the water mass containing the "oil fog" during its 2-3 hr movement between samplings.

Finally, when the *Jack Fitz's* ROV was in the middle of an oil layer, a very strong sonar return was noted from the ROV's standard 670 kHz sonar system (Figure 11). Typically, no signals were observed using a lower-frequency, 300 kHz ROV-mounted system or in clean water. This observation is relevant to understanding unsuccessful attempts by BP to detect oil lenses using surface-operated, low-frequency, sonar systems. Higher-frequency (shorter wavelength) sonar signals are necessary to resonate with small oil droplets, but they have a very short range (only several hundred m). Lower-frequency sonar signals can penetrate seawater to the greater distances required from surface-mounted systems but the longer-wavelength sound passes through the oil droplets with no reflectance (the oil is invisible). Thus, when lower-frequency sonar signals (with greater depth penetration) were used from surface-mounted ship systems, the effort was futile; no oil could be detected. Such systems are reasonably good at detecting gas plumes due to larger density differences between gas and water and thus, stronger returns. Surface-mounted, higher-frequency sonar systems did not have the range to penetrate to the depths of DWH oil plumes.

With these combined-package systems, it was possible to identify sub-surface oil lenses with real-time data received on the ship(s), and then sample above, below, and in the center of the DO and fluorometer anomalies. This approach was successful during and following the Deepwater Horizon event in helping to define the vertical and lateral extent of the subsurface deepwater plume and allow collection of dissolved- and particulate-fractions to understand the effects of *in situ* dispersant injections at the wellhead on oil-weathering processes at depth (Payne and Driskell 2015a, 2015b, and 2015c). In 2010, over 5,300 water samples were obtained for NRDA investigations using adaptations of these and other systems.

New advances have also brought portable field spectrometers to the effort, both in the ship's lab and at depth, installed onboard a submersible (Camilli et al., 2010, MBARI, 2010, Ryan et al., 2011, Bejarano et al., 2013).

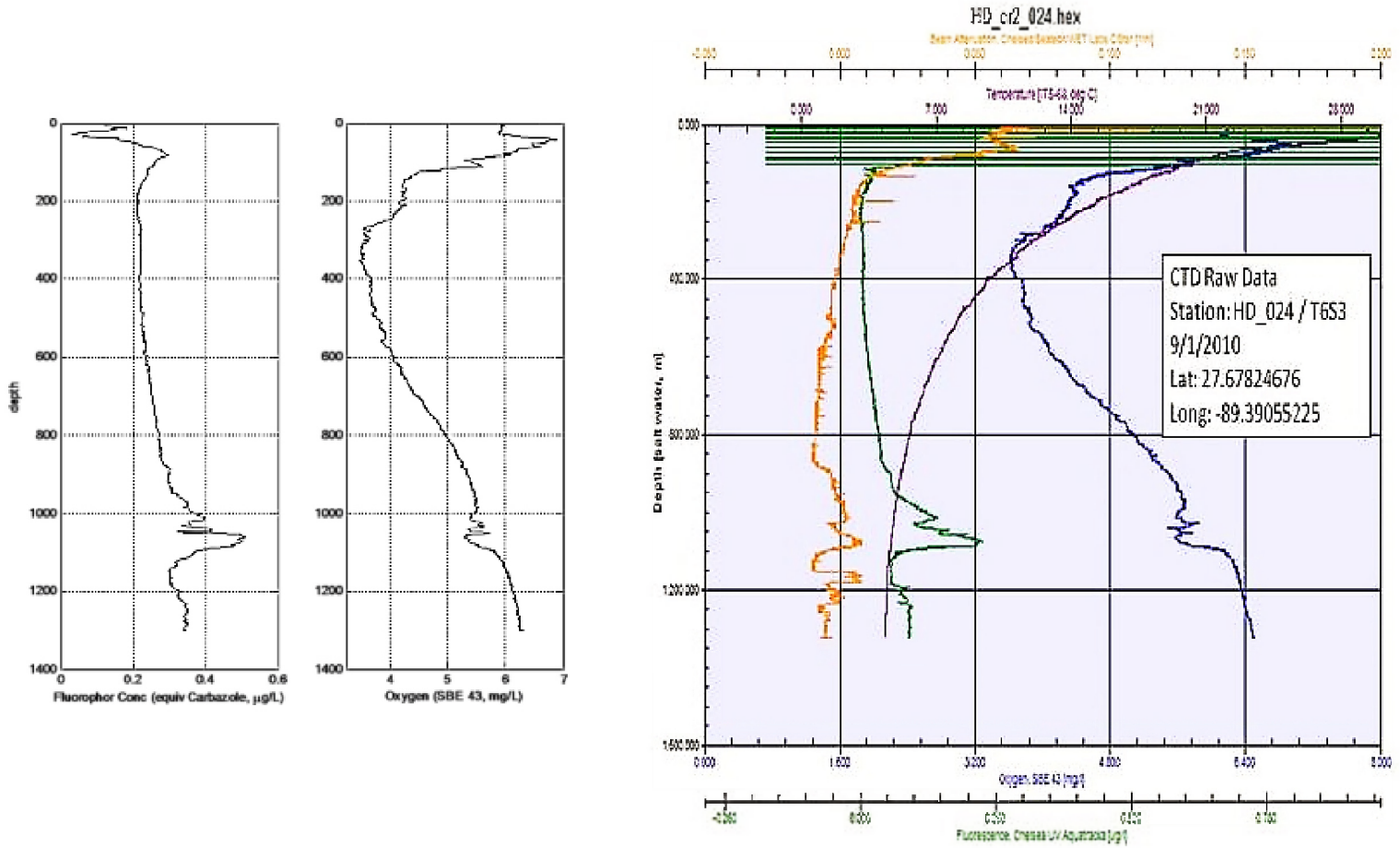


Figure 10. Comparison of DO and AquaTracka instruments between vessels. AquaTracka (fluorometry) and DO data on left collected by the *NOAA vessel Pisces*; data on right are from the *HOS Davis* corrected CTD, DO (blue), AquaTracka (green), and transmissometry(orange) at the same station approximately 2-3 hours later.

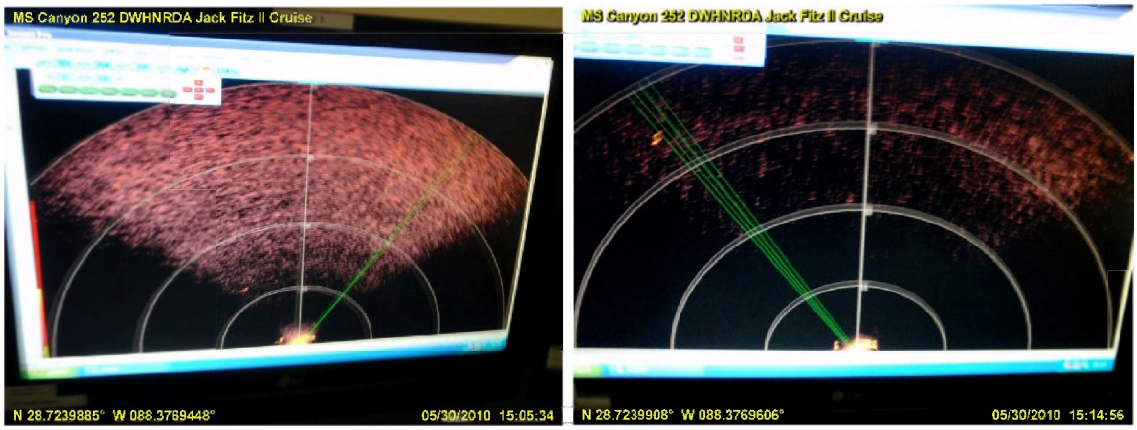


Figure 11. ROV-mounted 670 kHz sonar signal returns in the middle of the heavy subsurface oil plume at 1083 m (left) and in lighter (and smaller droplet size) oil plume at 1190 m (right). All photographs obtained at the same station as Figure 6 and Figure 7. Display marker rings in plots increment in 25 ft (7.6 m) segments.

Following the *Jack Fitz 3* cruise, BP commandeered all vessels for its independent Broader Gulf of Mexico (BGOM) offshore sampling program (Leg1 July 9-24). The hiatus removed access to the optimally configured vessels of opportunity and disrupted the time line of NRDA sampling, which was not to resume until the *Hos Davis* cruise(s) in August-December of 2010.

Sampling surface sheens and slicks

Surface sheens and slicks are both matrices of interest and potentially major confounding issues for water sampling. Sampling approaches can be as simple as bucket casts (empty buckets scooped by hand or on a line dropped over the ship's rail) or using pre-cleaned Teflon® nets (often deployed affixed to the end of a long pole or cast into the slick using a fishing pole arrangement). When planning for this usually opportunistic sampling, it is important to pre-consider the freeboard of the vessel such that the rope or pole can actually reach the water.

And observing a good sample is different from collecting a good sample. A thick slick or mousse may appear opportune but in approaching it, the prop wash from stern or bow thrusters or waves reflected amidships pushes the oil away. Given time, stopping downwind of the slick may bring the sample to the vessel where it can be carefully collected (as long as the vessel is not rolling excessively in which case reflected waves off the side will again push the oil away). Of utmost importance, the sampler must always be aware of potentially cross-contaminating vessel activities such as bilge discharges, stack exhausts blowing toward the surface oil or sample processing area, and deck wash containing hydraulic oils, lubricants, and equipment decontamination rinses draining into surface waters. And finally, when trying to collect a surface sheen, it is important to be aware of any potential emissions from a vessel's "bathtub-ring" of oil acquired from earlier surface-slick encounters.

During the *Jack Fitz 3* cruise in mid-June 2010, discrete oil droplets could be observed surfacing and breaking into rainbow-colored and silver sheens in clean water at down-current distances ranging from 1.5 to 4 km from the wellhead. These were successfully collected well away from the side of the vessel using Teflon nets cast out onto the open water with the fishing pole approach, and one such sample (JF3-2km-onet-20100616-surf-N143) collected in freshly surfacing oil 2 km north of the wellhead on 16 June 2010 (Figure 12) provided the "freshest" (least weathered) surface oil sample forensically characterized by Stout (2015a) in his analysis of over 60 floating slicks, mousses, and sheens collected between 10 May and 20 June 2010.

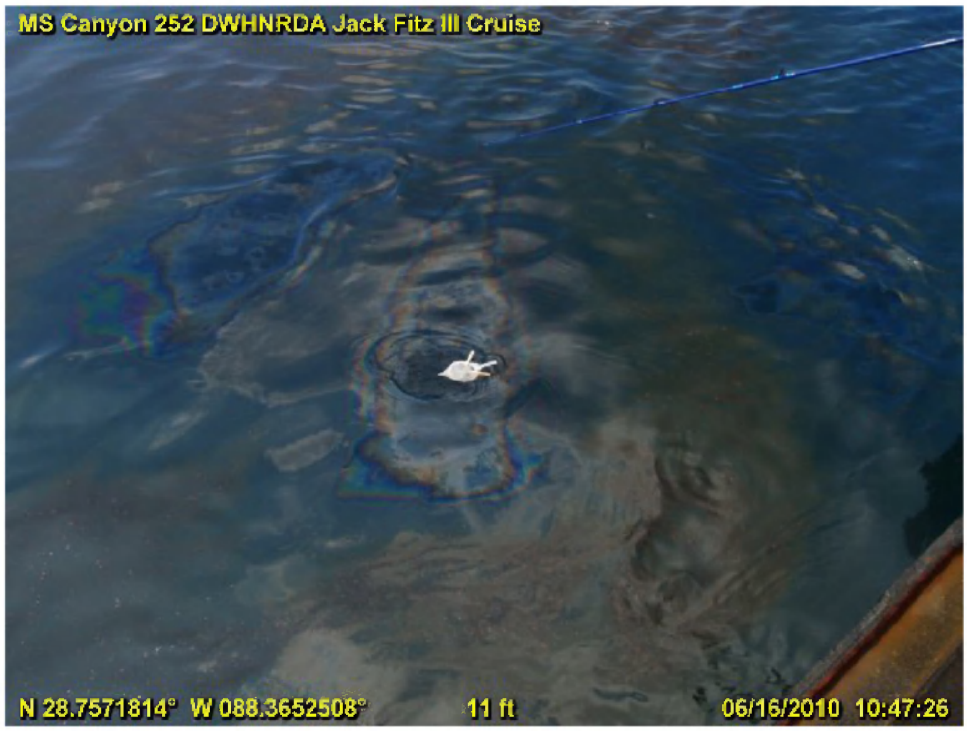


Figure 12. Rainbow sheen observed from rising oil droplets bursting immediately upon reaching the water surface at a station 2 km due north of the wellhead on 16 June 2010. The white ring holds a Teflon net being dipped via fishing line and pole directly into the rainbow sheen just as it was beginning to spread.

Besides being objects of sampling interest, surface slicks and sheens are also obstacles for subsurface water sampling. The next section considers how a sampling device can be passed through an oiled-surface interface without becoming contaminated.

Sampling equipment designed for subsurface water collection

Sampling gear designs for collecting water have been fine-tuned over the years such that most investigators routinely use Niskin or GoFlo® bottles but there are alternate methods, each with its advantages and issues. For oiled water sampling, the GoFlo sampler is preferred as it avoids becoming contaminated by passing through a potentially oiled water surface with the end ball-valves closed. Once beneath the surface, the ball-valves are triggered open by a hydrostatic pressure activator (usually ~10m below the surface) to descend open with a free flow of water through the bottle until retriggered at the desired sample collection depth. Niskin bottles are cocked open on deck and pass open through the potentially oiled, water surface. Both Niskin and GoFlo bottles are available with a Teflon® lining to minimize plasticizer (phthalate) contamination from the PVC construction materials. The Teflon lining is believed by some to also reduce the potential of oil-film adhesion to the interior of the bottle during draining, but to our knowledge this has not been tested.

Near surface water samples

To capture a near-surface water sample, e.g., 0-1m beneath a slick where dissolution or re-entrainment from surface slicks occurs, it is possible to deploy a GoFlo bottle as described above, and after initial opening at ~10 m, bring the bottle(s) back to the surface and take the sample. Because the bottles are

approximately 1 m long, however, depending on the pitch and roll of the sampling vessel, such samples are really a composite of near-surface (1-2 m depth) water. During the *Deepwater Horizon* event, extreme care was exercised to ensure that the sample bottle didn't break the water surface (particularly in areas where heavy oil or sheen was present).

Another major consideration when trying to collect near-surface water samples from a pitching or rolling boat is the reflected waves and backwash from the side of the vessel. The wave action and any turbulence from bow thrusters can push the oil away from the side of the boat or drive the surface oil deeper into the water. This effect was observed at the end of the *Jack Fitz* 1 cruise when Entrix was completing rosette and bucket casts for surface-oil/water toxicity testing on the windward side of the vessel in waters where the slick had been displaced. The chief scientist stopped the sampling operation and had the vessel turn 180 degrees such that the davit and hydrowire were then positioned on the leeward side. Under these conditions, the oil was observed much closer to the side of the vessel, and the casts for the tox tests resumed. Later forensics analyses revealed that the TPAH concentrations were two-times higher for particulate-oil fractions and seven times higher for the dissolved phase when the samples were collected from the leeward side.

In other circumstances, when trying to avoid surface oil slick contamination during sampling gear deployment, it is possible to take advantage of the vessel position and "holes" blown into the slick by the bow thrusters, or use other techniques to minimize sampling artifacts. Obviously, an open Niskin bottle that gets oiled on the surface is compromised. Unopened GoFlo or even sensors that get oiled externally may carry oil into unoiled depths and create a false positive sample. Coated sensors will likely malfunction, and bringing heavily oiled gear into the onboard sample processing area is inviting compromise.

Three approaches to avoid these issues have been used with varying success. The first method is to break an entry through the slick or sheen using a jet of water from the vessel's deck hose. The constant jet of the hose can break the surface tension of the slick and create an adequate sized entry. The only concern is that the jet can also introduce droplets into the shallow water. In this context, the decision must be made as to whether the near surface depth should be sampled upon entry or after deeper waters have been collected (i.e., as the last sample on a cast before equipment retrieval). Consideration must also be given as to how near the surface to bring the bottles to double-check their open/closed status. Generally, on entry, the hydrostatic release on a GoFlo bottle will open at around 10 m, and then the sampling array is brought up to a shallow-enough depth to visually confirm the bottles are open and operationally ready but deep enough to avoid breaking the surface in a wave trough.

The second method suitable for sheens and thin slicks on calm water is to apply a squirt of dish detergent to the water surface to break the oil's surface tension. Due to the herding effect of the surfactants in the detergent, a surface entry immediately springs open and holds until the soap eventually disperses and surface tension is restored. If the analysis plan includes dispersant products, however, the selected brand of detergent should not contain the active surfactant in the dispersant, typically dioctyl-sulfosuccinate (DOSS) or a secondary analyte of concern (glycol ethers for GC/MS methods). Neither Alconox® laboratory cleaners nor Dawn® brand detergents (except Dawn Degreaser®) contain DOSS.

A third method was used during the *Exxon Valdez* spill as a diver portal through slicks. First, a squirt of detergent opens the slick. Then, a ring of absorbent boom is dropped into the opening and expanded to keep the slick from reclosing. Divers then have a reasonably oil-free entry and exit through the slick. Although suggested, it is unknown whether this method was used during the DWH sampling.

Deeper water samples

As previously mentioned, most investigators during the Deepwater Horizon NRDA cruises routinely used Niskin or GoFlo bottles either hung individually on a hydrowire or more often, mounted as multiples in a rosette frame. Typically, the rosette was used with electrically conductive hydrowire that permitted

remote triggering at the sampler's discretion. Going beyond simple water collections, remotely-operated vessels (ROVs) and both manned and autonomous submersibles were also outfitted with field spectrometers and employed for analyzing and collecting water samples (Camilli et al., 2010, MBARI, 2010, Ryan et al., 2011).

Heterogeneity of oil in large Bottle Samplers

Due to the oil's buoyancy, any free droplets less dense than water tend to rise. This implies that any suspended particulate oil (i.e., free oil droplets), given time, will be in a non-homogeneous distribution within a sample container. Hence, when captured in a large GoFlo or Niskin sampling bottle while operating at sea, in the time it takes to retrieve and process the sample, the droplets will tend to rise to the top and form a meniscus (Figure 13).

Thus, when a bottle aliquot (subsample) is drained via the bottom sampling valve on the GoFlo/Nisken bottle into a 1 liter glass jar, the first liters out of the sampling bottle will be missing their portion of particulate oil that has risen higher in the bottle. More specifically, most droplets have left the bottle's bottom 4.2 L volume (0.2 L of VOA samples plus 2 L each for Trustee and RP splits) in 10-30 minutes. In most shipboard scenarios, sampling personnel could not have retrieved nor processed the set of samples within this short interval. During forensic analysis, samples showing obvious anomalies (strong DO and fluorescence signals at the sampling depth, but no or very low measured TPAH concentrations) were designated as FBOBs (from bottom of bottle).

Figure 13. Oil film meniscus forming on water surface within a GoFlo Bottle (top view looking downward).

As a result of this observation in the field, an adaptive subsampling protocol was employed whenever the Payne Portable Large Volume Water Sampling System (PLVWSS) was used to process and filter seawater samples. Specifically, during sample processing, the FBOB issue was partially mitigated by first

collecting non-filtered aliquots and sample splits, usually a combination of VOAs, dispersants, TSS, and 1 L whole water aliquots for BP and the Trustees. Then, the remaining calculated volume in the GoFlo bottle was metered out (when necessary actually draining and discarding excess, e.g., most of any 20 L GoFlo bottles), keeping only the last, upper ~3.5 L aliquot, thus ensuring that any oil meniscus (free-floating oil) was captured for filtration samples.

Models of rise time using distributions of droplet sizes in the DWH plume estimate 95% of the droplets have completely ascended to the top of the bottle within 40 minutes (varies with bottle dimensions; Figure 14). Similar, but inverse aliquoting issues have been reported with collecting water samples for suspended particulate material (SPM) analyses, when the sedimentary material tends to settle out of the collection devise (Feely et al., 1991). With inorganic materials, the SPM can sometimes be resuspended by vigorously inverting the sampling bottle before aliquot removal, but this was impractical during DWH sampling because of (1) the sampler size and weight (particularly with 10 and 20 L GoFlo Bottles), (2) their being securely mounted either in rosettes or to the ROV's TMS, and (3) once oil formed a meniscus at the top of the bottle, no amount of turbulence could be introduced by shaking or inversion to re-distribute the droplets long enough to facilitate sub-sampling.

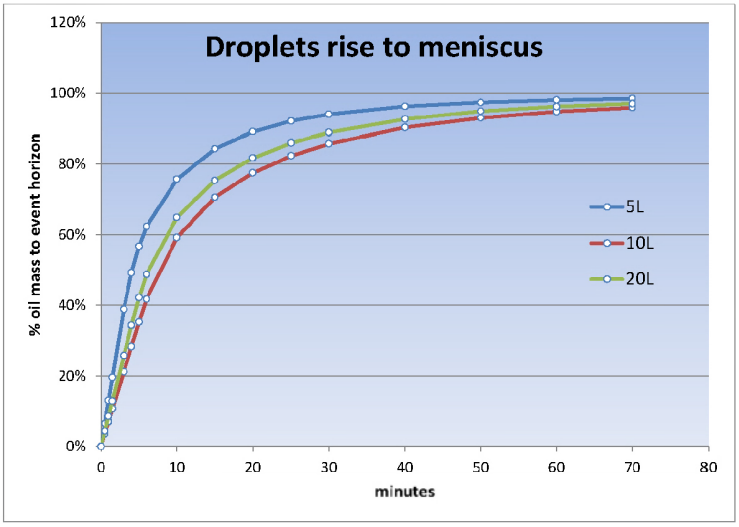


Figure 14. Mass transfer of oil to meniscus in lapsed time since capture in various GoFlo bottle volumes. Note that because of similar dimensions, 5 and 10L Niskin bottles rise times are nearly identical to 5 and 20L GoFlo bottles.

In summary, every sample from the bottom of a GoFlo or Niskin bottle will likely incur an underestimate of particulate oil. This effect was seen in some DWH samples where duplicates were analyzed and also in circumstances where 1 L whole water aliquots were taken prior to the top 3.5 L collections for filtration. On the other hand, every 3.5 L aliquot taken from the top of the bottle will have an overestimate of particulate oil (since those particulates actually comprise all of the original sample volume of 5, 10, or 20 L) but within calculable limits from 1 to 5.7x excess.

Water Samples of opportunity

Observed oil droplets surround by mucus agglomerates

During the *Jack Fitz* 1 cruise (9-15 May 2010), we planned to initiate our sampling effort in clean water (nominally up-current from the wellhead) and then work our way closer to the wellhead collecting samples at 8, 4, and 2 km from the source. Unfortunately, aerial support was not available to assist in

this effort, so based on wind and current data collected before the cruise, we elected to start sampling at a planned "reference" station 12 km north-east of the wellhead. When we arrived at this station on 10 May 2010, however, there was surface oil, mousse, and sheen everywhere (Figure 15), so after several bucket casts to collect surface mousse, we elected to pass on any water-column sampling and continued to the east-north-east in search of clean water.

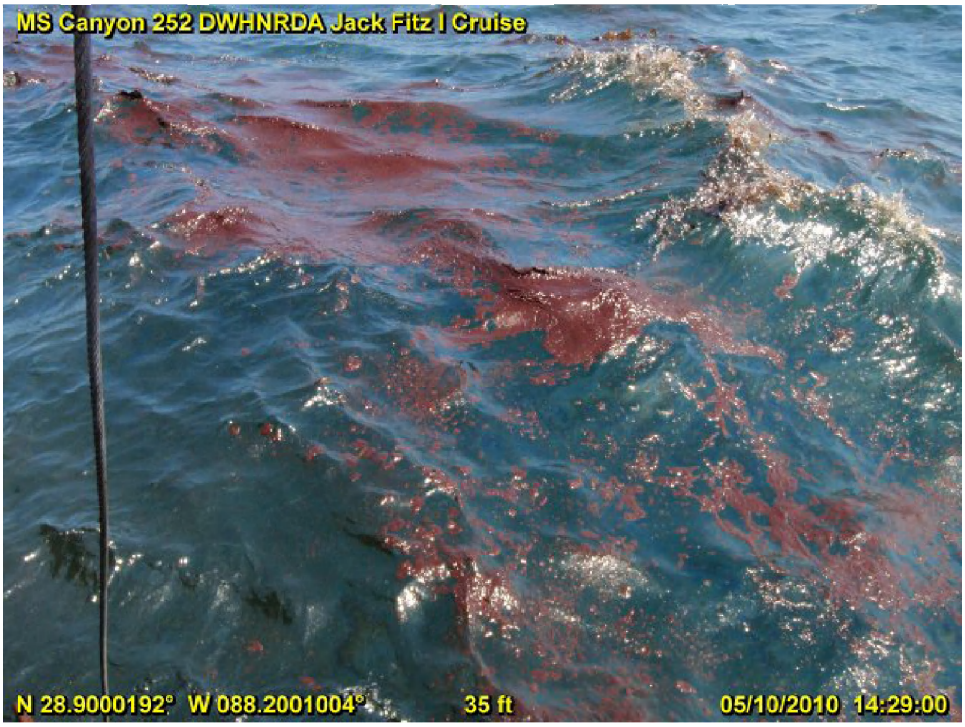


Figure 15 Oil and mousse at the original (planned) *Jack Fitz* 1 reference station 13 nm NE of the wellhead.

After almost 18 hours of steaming in search of clear water, we arrived at a "new reference" station 28 nautical miles NE of the wellhead the following morning, but even at this location (~74 nautical miles south of Mobile, AL), water-borne oil contamination was much more extensive than we had anticipated. Patches of sheen, surface scum, and what appeared to be neutrally buoyant oil "flakes" in the upper 1 m of water were observed (Figure 16). Just the slightest wind or surface chop easily dispersed the surface oil/scum into the water, and a bucket cast allowed collection of these fine and suspended droplets. Upon standing undisturbed for 5-10 minutes these droplets would rise in the bucket to break into sheen (Figure 17), but when captured and examined under a microscope (Figure 18) it was evident that the droplets were entrapped in a mucus layer that maintained the agglomeration. The mucus encapsulation is slightly more apparent in another photomicrograph (Figure 19) taken the following day from a bucket cast of oil flakes in clear water 4 km from the wellhead[1]. Even after as few as 19-20 days from the initial blowout and fire, microbial processes were already at work on near-surface submerged oil droplets.

[1] A camera mount for the borrowed microscope was not available. As a result, the photomicrographs shown in Figure 18 and Figure 19 were taken by manually holding a camera over the microscope lens opening where the camera mount would normally be inserted.

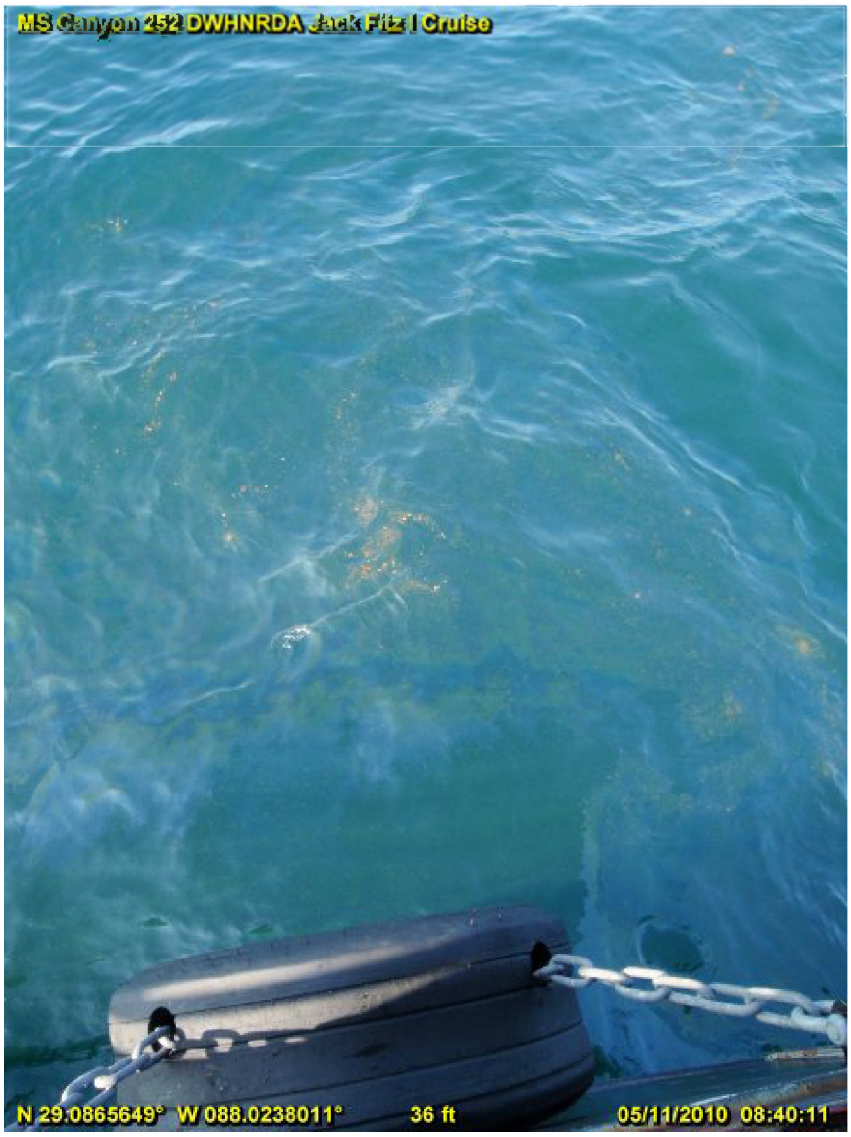


Figure 16 Surface scum, sheen, and oil flakes observed in the upper 1 m of water at the secondary *Jack Fitz* reference station 28 nautical miles NE of the wellhead.

Figure 17 Oil sheen forming inside a bucket grab of microscopic, near-surface neutrally-buoyant oil droplets after standing undisturbed for 5-10 minutes.

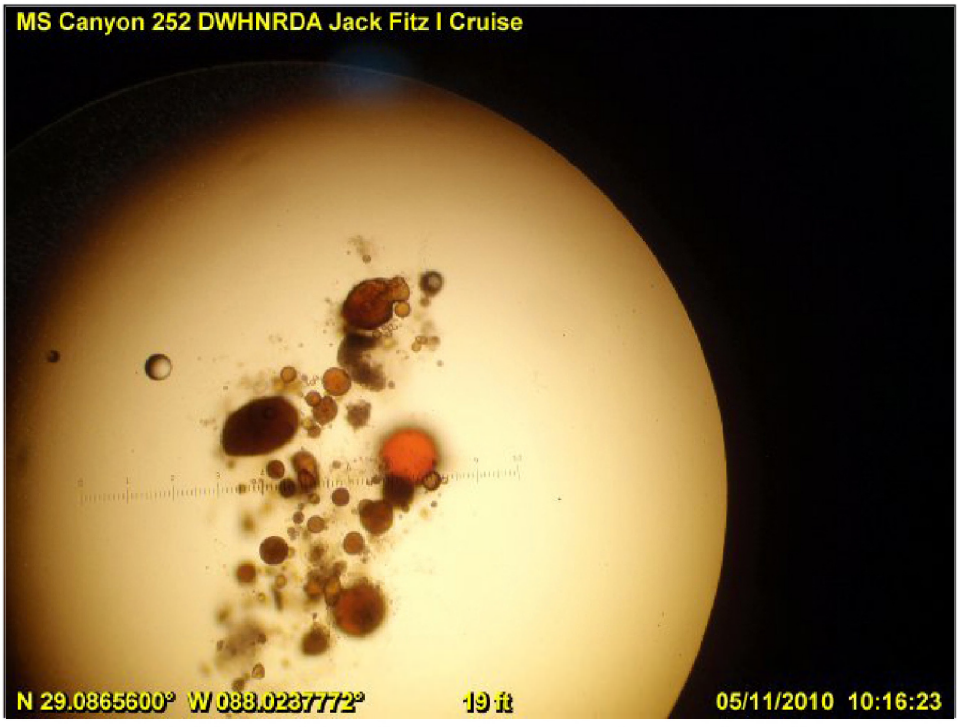


Figure 18 Photomicrograph of oil droplets/flakes collected by bucket cast at the "new reference" station 28 nautical miles NE of the wellhead. Each small division on the micrometer scale is 10 µm (the overall length of the scale is 1 mm).

Figure 19. Photomicrograph of near-surface oil droplets (~5-20 µm diameters) encapsulated in a mucus matrix collected from a 12 May 2010 bucket cast of clear water 4 km east of the wellhead.

Marine snow and microbial-mucus strings of oil observed at depth

On several occasions during the *Jack Fitz* 3 cruise (12-21 June 2010) when using the ROV to collect water samples at depth, large (0.5-1 m long) strings of mucus and entrained oil droplets were observed near the bottom at distances up to 9.5 km (5.1 nautical miles) NNW from the well head. These were very difficult to photograph because of the relative motion of the ROV and camera (Figure 20) but good video recordings were obtained at 1115 m that showed the stringers' scale, ephemeral nature, and near-neutral buoyancy against the back drop of the TMS. Later forensics analysis of the dissolved and particulate fractions from 1105 m and 1095 m confirmed DWH oil.

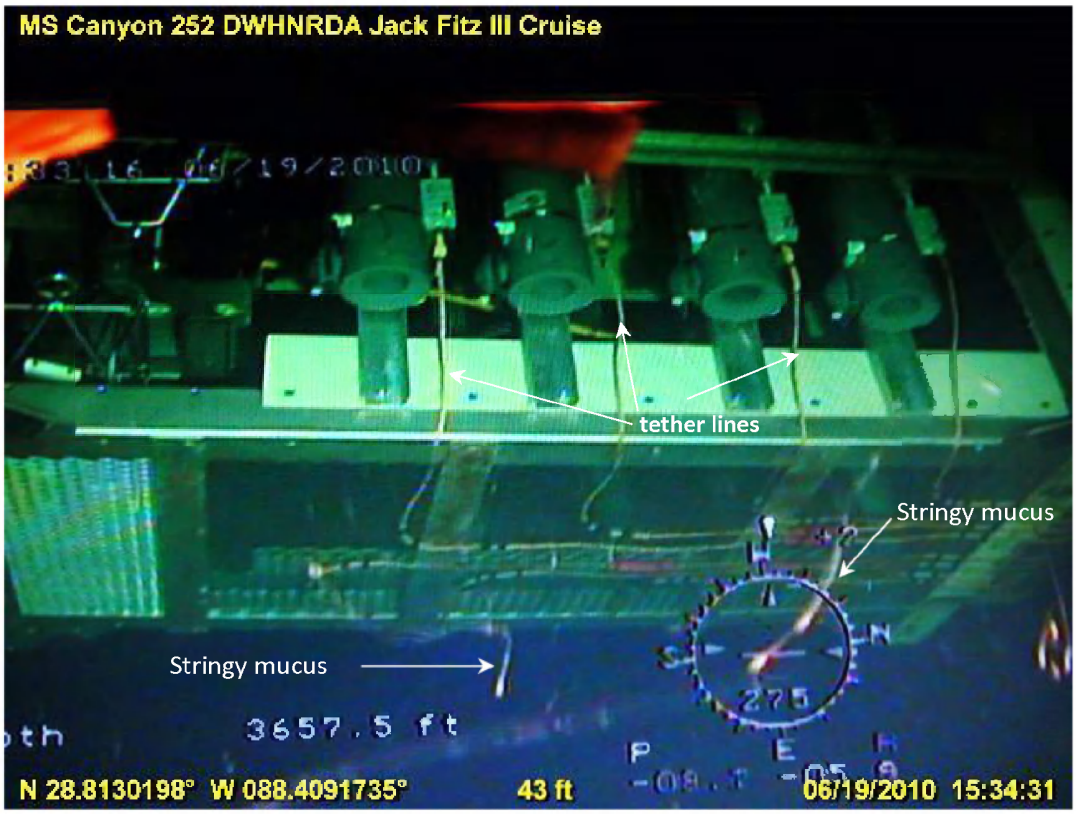


Figure 20. Stringy mucus floc photographed below the TMS cage (to the left of and behind the compass rose) at 1115 m depth and 5 nautical miles NNW of the wellhead on 19 June 2010. The tether lines used to trip the GoFlo bottles from the front of the ROV while still in the TMS are also shown.

Additional photographic and video files at this station showed stringy mucus filaments settling to the bottom (Figure 21 and Figure 22), and elsewhere, in the region (1.6 km NW of the wellhead), dead and decaying pyrosomes were observed accumulating on the bottom (Figure 23). It is unclear, as observers, whether these biota were felled from exposure to the dissolved or particulate fractions (or both).

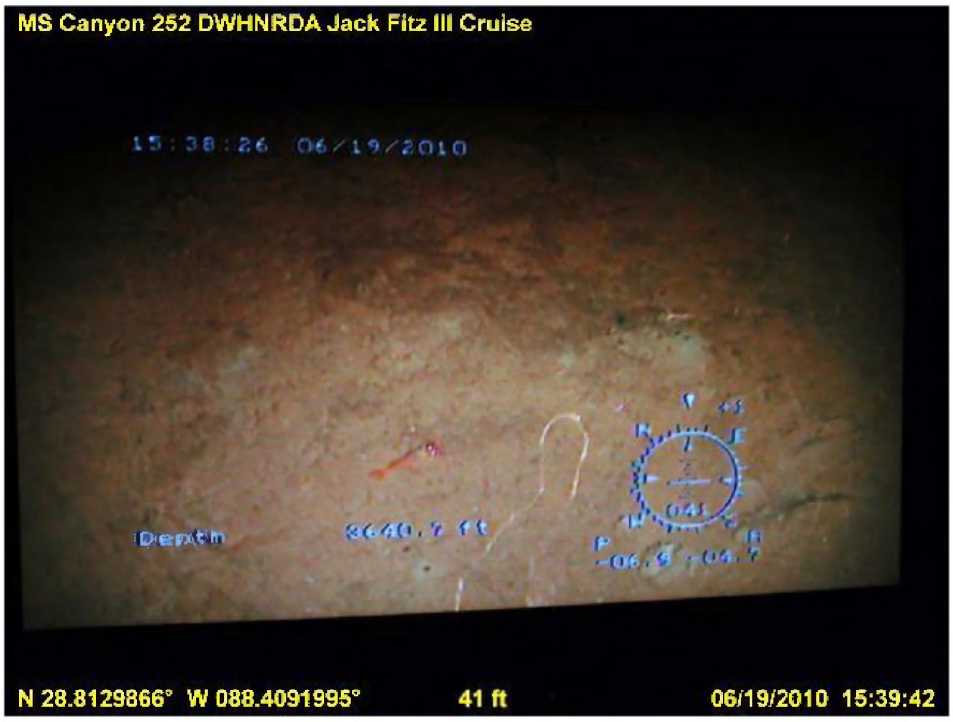


Figure 21 Stringy mucus and shrimp on the bottom sediments 5 nautical miles NNW of the wellhead.

Figure 22. Mucus/oil strings floating just above the sediment 5 nautical miles NNW of the wellhead. The blurred images are due to water movement as the ROV was "flown" just above the sediment/water interface and better documentation was obtained through video recordings.

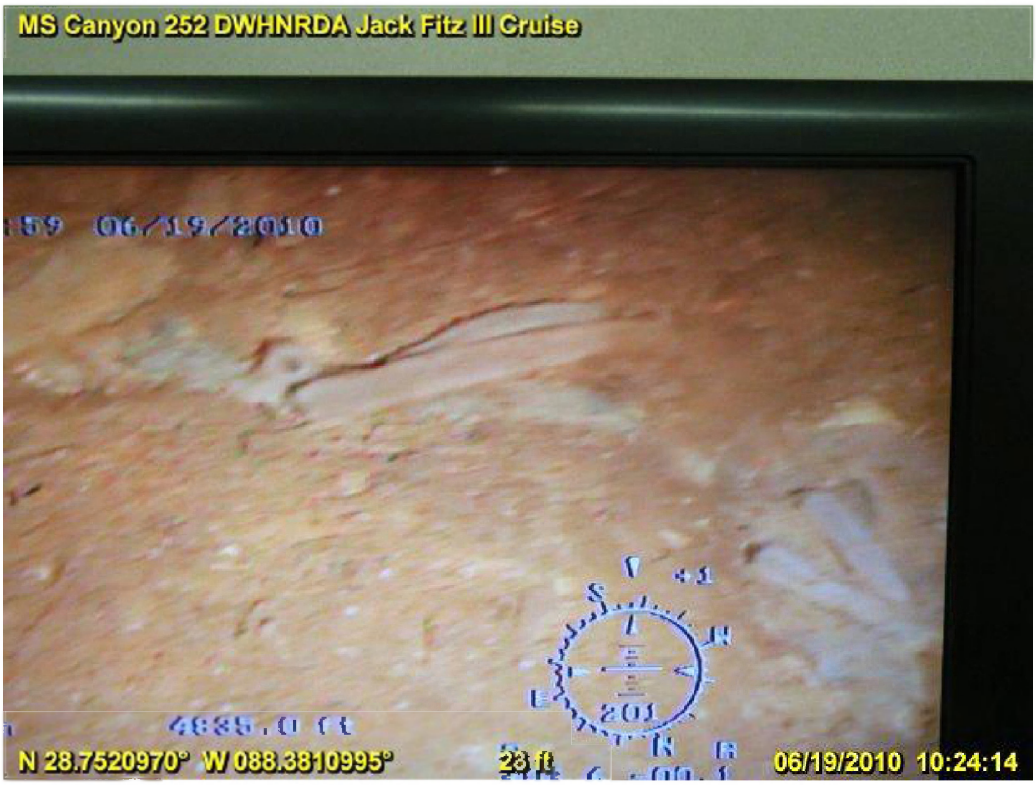


Figure 23. Dead and decaying pyrosomes littering the bottom 1.6 km northwest of the wellhead less than a month after the initial blowout.

Sediment Sampling with an ROV

During the May and June *Jack Fitz* cruises and subsequently during the late-August through December 2010 *HOS Davis* cruises, there was additional photographic and video evidence of unconsolidated flocculent material accumulating on the bottom sediments, but this ephemeral layer proved very difficult to sample. Just the slightest turbulence from movement of a sediment core barrel near the sediment-water interface would resuspend and scatter it (Figure 24). With practice and meticulous diligence, the ROV on the *HOS Davis* was eventually successful in collecting the first fine-sectioned sediment cores (with samples isolated from 0-1, 1-3, and 3-5 cm layers), but the flocculent layer still proved to be somewhat elusive. During the same period, BP and scientists on some response cruises were using large multicore samplers to collect 0-3 cm sediment composites; based on our experience, we suspect that the sampler's bow wake inevitably blew away most of any recently settled oil or oiled suspended particulate material (SPM) that may have settled to the bottom.

Furthermore, by compositing the upper 0-3 cm on those cruises, any recently settled material, only a few mm thick, would be heavily diluted by the background signals deeper in the core. From finer-sectioned NRDA samples, Stout (2015b) observed significant depth gradients with *Deepwater Horizon* oil in the uppermost 0-1 cm layers and other contributing sources deeper in the cores from many of the *HOS Davis* and later (2011) *HOS Sweet Water* samples.

Figure 24. Surface-floc resuspension due to slight core-barrel movement during aborted attempt to obtain a sediment core sample in a *Beggiatoa* microbial mat during the *HOS Davis 3* (8-28 September 2010) cruise.

ROV Slurp-Gun Sampler

Based on lessons learned from the difficulties in collecting undisturbed floc with a core tube, a vacuum operated "slurp gun" was designed and mounted on the ROV for the 2011 *HOS Sweet Water* 2, 4, and 6 cruises such that the floc could be collected concurrently with the sediment and near-bottom waters. The slurp gun sampler utilized a carrousel to vertically hold separate cylinders or canisters for each floc sample collected by *in situ* vacuum filtration at depth (Figure 25 and Figure 26). Each cylindrical collection canister was equipped with a combination of sintered-metal and glass-fiber filters (Figure 25), such that when suction was applied from a submersible vacuum pump on the rear of the TMS, the collected water and floc would be trapped on the canister's bottom filter for later processing in the ship's clean room. In practice, the slurp gun used the suction wand (on red taped T-handle in Figure 26) that was swept by the manipulator arm of the ROV just across the sediment-water interface to collect any loose flocculent material into the sample chamber vertically held in the carrousel (Figure 26). After each sample was collected, the carrousel was rotated to the open chamber (not containing a sample canister) in order to flush clean seawater through the chamber and sampling hose. Additional details are presented below under Typical ROV Sampling Operations (p 41).

Sediment Coring Systems

During the *HOS Sweet Water* cruises, long (5-12 km) transects were typical, each taking 12-14 hours to complete, so the ROV sampling systems had to have secure, disturbance-free storage of sample collections before the ROV returned to the surface and the samples processed. As such, in addition to fabricating the slurp gun, a much more robust sediment coring array was required to facilitate sample collection.

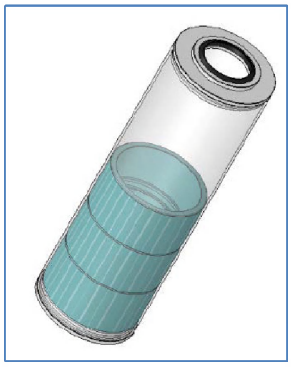
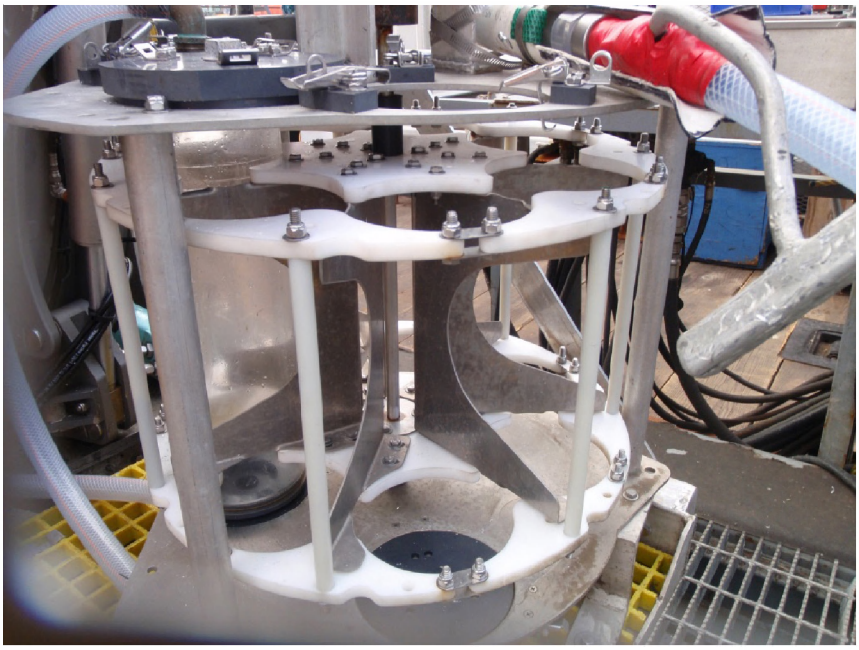


Figure 25. Slurp-gun canister design (left) with FEP inserts (blue) to hold a metal and glass-fiber filter array at the bottom (not shown) allowing flocculent material to be trapped during vacuum collection. Slurp-gun canisters and filter assemblies (right) being prepared in the clean-room on the *HOS Sweet Water*.



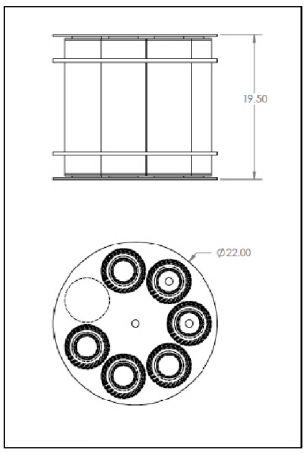


Figure 26. Slurp-gun carrousel showing empty slots for sample canisters and the open chamber (left side) for flushing the wand (red) and sampling tube between samples. For sample collections, the sampling hose is permanently attached to the gray-colored cap on the left side of the upper plate of the carousel holder while sample canisters (held in the white carrousel) are rotated to fit under it. Water is suctioned through vent holes in the bottom plate trapping floc and SPM on the glass-fiber filter housed in the bottom of the canister. Conceptual design (right) for the carrousel holding six canisters and the empty chamber (denoted by the dotted circle) for rinsing the collection wand and hose between samples (dimensions in cm).

On early *HOS Davis* cruises, sediment cores were laid sidewise in a collection box on top of the TMS, a practice that could resuspend the floc and/or mix any unconsolidated top layers. The disturbance issue was solved for the *HOS Sweet Water* cruises with an improved sediment core-sampling array that included a rack mounted in front of the TMS (Figure 27 and Figure 28). With this array, individual core-barrels could be readily withdrawn from a holster for video-camera assisted sediment coring and immediately placed back into their respective holster after sample collection by the articulating arm of the ROV (while still inside the TMS). Each labeled core barrel cap attached to the "T-handle" was designed with a one-way vent assembly such that water in the core barrel could escape through the top as the core barrel was pressed into the sediment. The vents then sealed as the core-barrel and contained sediment was withdrawn from the sea floor with internal suction then retaining the sample. Additional details are discussed below under operational considerations.

Figure 27. Sediment core barrel rack containing eighteen core barrels (and vented core-barrel handle assemblies) on the "front-porch" of the TMS. The six white circular floats adjacent to the core-barrel rack (by the technician's left hand) are tethers to GoFlo bottles at the back of the TMS allowing water sample collection by the ROV while still in the TMS cage.

ROV Sampling from Vessels of Opportunity

Remarkably, almost all of the NRDA water and sediment sampling efforts were completed on chartered vessels-of-opportunity (Figure 29 and Figure 30) rather than on the better-equipped and experienced academic- or institution-operated research vessels that were often tied up with other special-studies projects. Most vessels-of-opportunity used for the 35 plus NRDA cruises were converted mud-boats or industry supply boats with substantial, flat aft decks normally used for transporting drilling pipe, drilling mud, or other materials for the offshore oil and gas industry. Fortunately, most came equipped with bow thrusters to maintain dynamic positioning (DP) while on station, but all the scientific and oceanographic equipment (CTD winches, ROV/TMS winches and articulating A-frames, support trailers, generators, and even housing) had to be secured and welded to the back deck. Scientific personnel were bunked in the trailer units and a few available staterooms in the bow while the lower floor of a

Figure 28. ROV sampling assemblage comprising eighteen sediment core barrels in individual holsters plus two empty holsters (with caps) for biological samples and the slurp-gun carrousel mounted on the front porch of the TMS. The white ring-floats to the left of the core-barrel rack are attached to tethers for triggering GoFlo bottles mounted on the back of the TMS (not shown).

two-story Martin Quarters was set up as the science operations center (Figure 30). Separate trailers were used for ROV operations with all the scientific support trailers and the bridge interlinked with a closed-circuit TV and communications systems. Although crowded and appearing a bit ad-hoc, the integrated systems worked amazingly well, and some world-class oceanography was successfully accomplished.

Figure 29. *HOS Sweet Water* supply boat chartered to serve as a "vessel-of-opportunity" for the 2011 NRDA near-bottom-water, sediment, and floc sampling programs.

Figure 30. Oceanographic equipment secured to the rear deck included two air-conditioned two-story crew quarters (with the science lab occupying the lower floor of the white Martin Quarters unit on the right), a walk in "clean lab" (white trailer on left) for sediment core and slurp-gun sample processing, the TMS A-frame launch and recovery system (LARS) (aft of the clean lab), the TMS lab and control center (the two white trailers aft of the LARS and yellow TMS/ROV unit), and other assorted trailers, generators, and conex container boxes used to support the scientific mission.

With the ROV fully configured with the systems described in the previous section, it was deployed from the *HOS Sweet Water* (Figure 31 and Figure 32) to collect near-bottom water, floc, and undisturbed sediment samples along hundreds of kilometers of bottom transects near the MC252 release site, the surrounding basin, and adjacent salt domes. During cooperative cruise planning, proposed sampling transects were laid out to look for *Deepwater Horizon* oil residues in areas where fallout plume deposits may have occurred within the surrounding basin and along the slopes of the adjacent salt domes to investigate the possibility that advected oil in the deep plume may have left a "bathtub ring" of oil around the area (Figure 33). After five *HOS Sweet Water* cruise legs between March and November 2011, thousands of samples had been collected, and those exhibiting traces of oil as manifested by a faint petroleum odor or a silver/colored sheen on top of the supernatant water above the core or slurp-gun sample are designated with a yellow circle on the overview map (Figure 34). Eventually, by the end of 2011, near-bottom water, floc, and sediment samples were collected from several hundred kilometers of transects that were located over 104 km (64 miles) to the north-east (head of DeSoto Canyon) and 180 km (110 miles) south-west of the well head.

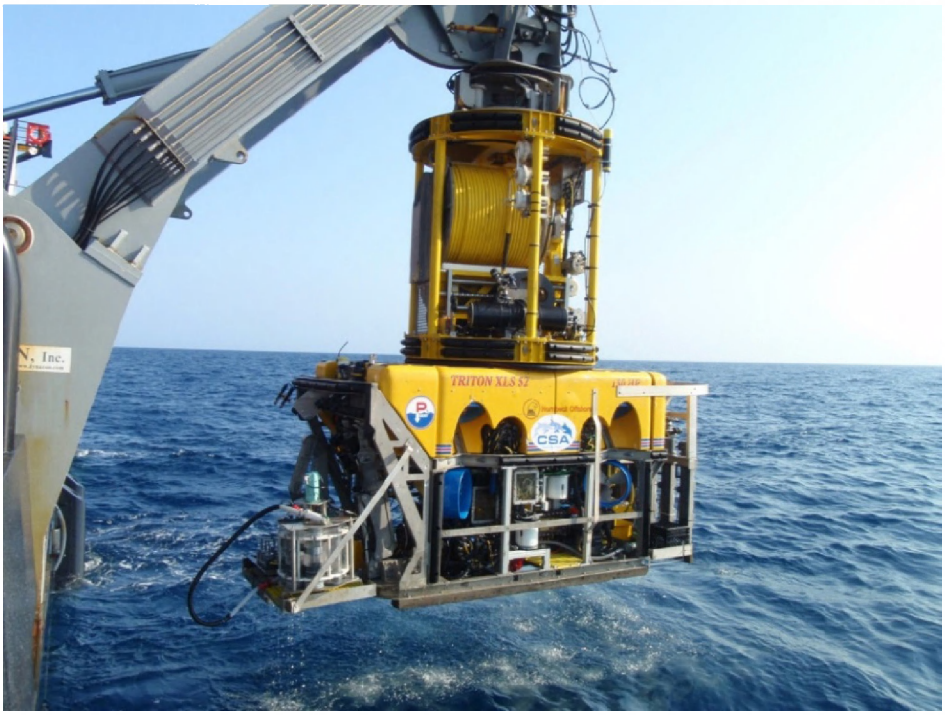


Figure 31. Triton XLS 52 TMS and ROV as configured for the *HOS Sweet Water* cruises. The sediment core-barrel rack and slurp gun with its sampling wand are on the left (front) side of the TMS, and the 10 L GoFlo bottles can be seen within the protective bumper guards on the right (back) side of the assembled system. Note that with all this extra equipment, additional syntactic foam was necessary to maintain near neutral to just slightly positive buoyancy.

Figure 32. CTD/AquaTracka fluorometer, six 10 L GoFlo bottles, and closed-circuit TV camera housed within a bumper-cage on the back of the Triton XLS-TMS and ROV used on the *HOS Sweet Water*.

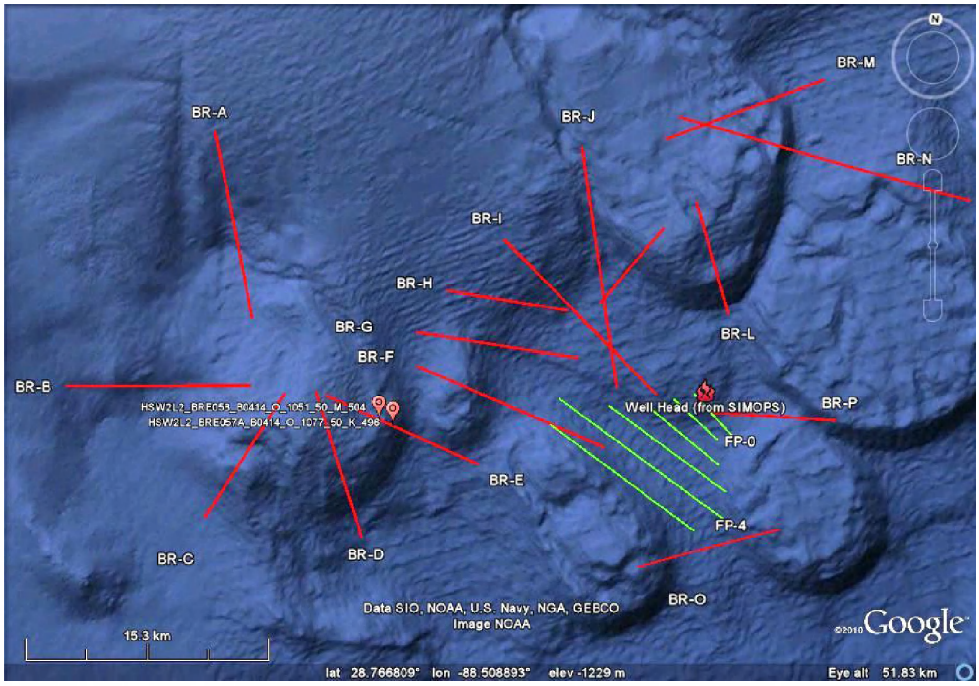


Figure 33. Proposed Fallout Plume (FP -- green) and Bathtub Ring (BR -- red) transects laid out in the cooperatively-prepared *HOS Sweet Water 2* cruise plan.

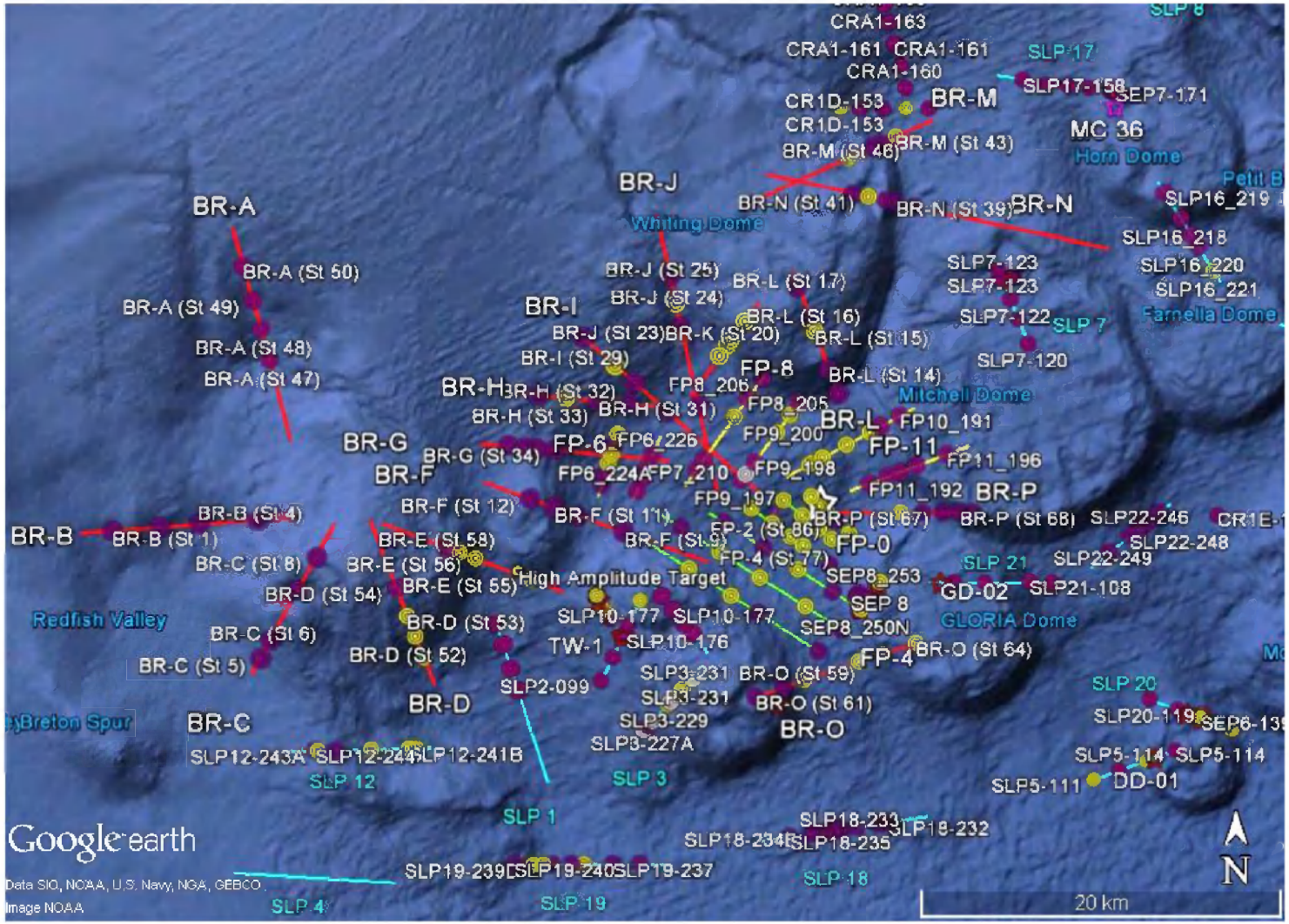


Figure 34. Completed station locations along Fallout Plume (FP) and Bathtub Ring (BR) transects at the end of the five *HOS Sweet Water* cruise legs completed between March and November 2011. The MC 252 wellhead is identified by the white star, and the yellow highlighted stations exhibited petroleum odor and/or visible oil sheens in the slurp gun samples or supernatant water collected above the ROV-supported push-core sediment samples. Sediment sample forensics are discussed by Stout 2015b.

Typical ROV Sampling Operations.

During cooperative BP-Trustee preparation of each HOS Sweet Water cruise plan, the starting and ending coordinates for each transect were pre-selected based on location relative to the wellhead and bottom bathymetry as delineated on Google Earth maps. Areas of suspected fallout plumes, the sides of the surrounding salt domes making up the basin, and control areas further from the wellhead were each selected to assess potential sediment impacts. Pre-planning each transect at sea, the Chief Scientist would plot the selected transect and include the bathometric profile to evaluate potential depositional areas, depressions or relatively flat spots; locations where sampling would be targeted (Figure 35). Those coordinates would then be entered into the HYPACK navigation system (version 2011) used by Continental Shelf Associates (CSA) personnel to coordinate vessel movements along the transect with the bridge. Copies of the planned cruise track would be placed in the Science Ops trailer above the operating station and in the ROV control room to inform the ROV pilot and articulating-arm operator of the relative length of the transect, its location relative to the wellhead or salt-dome features, and the anticipated changes in bottom depth.

The ROV/TMS would then be deployed several hundred meters down-transect from the coordinates for the deepest station along the route. Once near the bottom (~0.5-1 m above the sediment/water interface), the ship was directed to begin moving up the transect (toward shallower stations) at approximately ½ to 1 knot. The ROV pilots/operators (Figure 36) would "fly" the ROV/TMS along the bottom (it was not towed by the LARS umbilical running back to the ship) while science support personnel and the vessel captain monitored the TMS location relative to the ship and the planned transect line via the on-screen displays (Figure 37) in their respective locations (ROV trailer, science trailer, and the bridge).

Typically, a standard protocol was followed during each near-bottom transect. Forward-looking, closed-circuit TV and on-board sonar returns were used to watch for obstacles (e.g., pipelines, rock outcrops, etc.) or interesting features that might warrant further investigation and sampling (discussed below). Then, when approaching a pre-selected station (Figure 37), the ship would slow and hold station (on DP). While at stop, the ROV collections began, first, taking a near-bottom water sample with the GoFlo bottles on the rear of the TMS prior to disturbing the sediments. The ROV/TMS system was equipped with sufficient syntactic foam so that it always had slight positive buoyancy. This allowed it to be positioned just above the bottom using only the top mounted TMS thrusters pushing down, ensuring that prop turbulence was above the vehicle and that no sediment was resuspended. Above the GoFlo bottles, a closed-circuit TV camera monitored the bottom (Figure 38). Typically, the bottles were tripped about 0.5 m above the sediment, just before any fines or flocculent material was disturbed. If some inadvertent sediment resuspension was observed, the whole system would be "flown" forward until in clear water again. The bottles were tripped by using the ROV manipulator arm to pull the tether attached to the numbered floats just to the right of the sediment push-core rack (Figure 39) while the open/closed status of the bottles was monitored by observing the position of the ball valves on both the bottom and top of each bottle with the closed-circuit TV (Figure 38 and Figure 40).

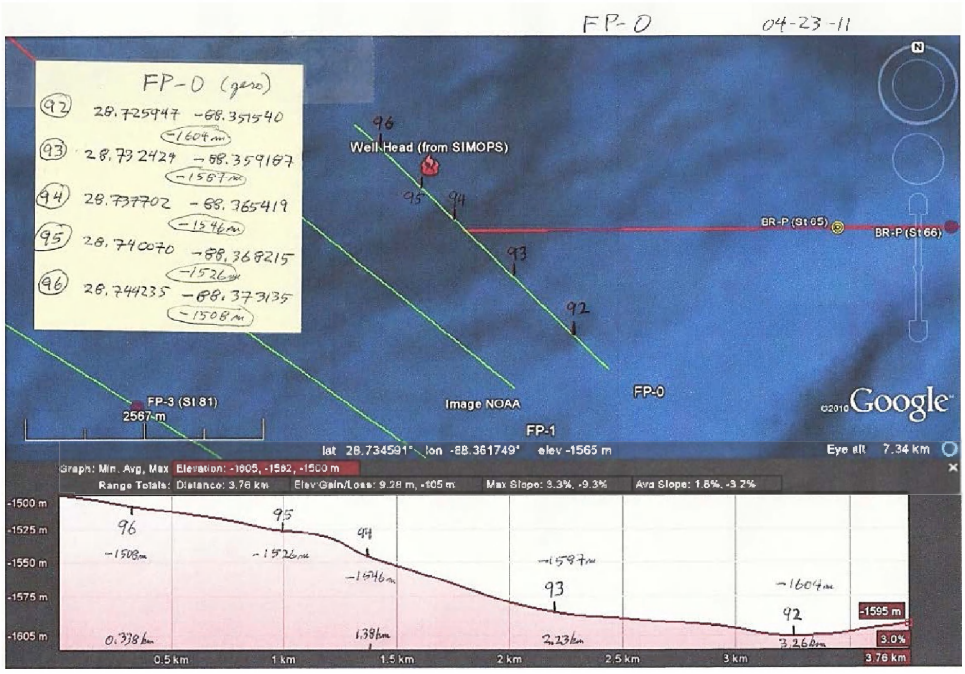


Figure 35 Transect FP-0 (fallout plume closest to the wellhead) sampling plan with Google Earth, along-transect bathymetry and hand-drawn station locations and depths noted. Pre-planned station IDs, coordinates, and depths were entered into the ROV's HYPACK navigation system before each dive.

Figure 36. ROV pilot, Paul Sanacore, and manipulator-arm operator at the control panel within the ROV trailer on the *HOS Sweet Water*.

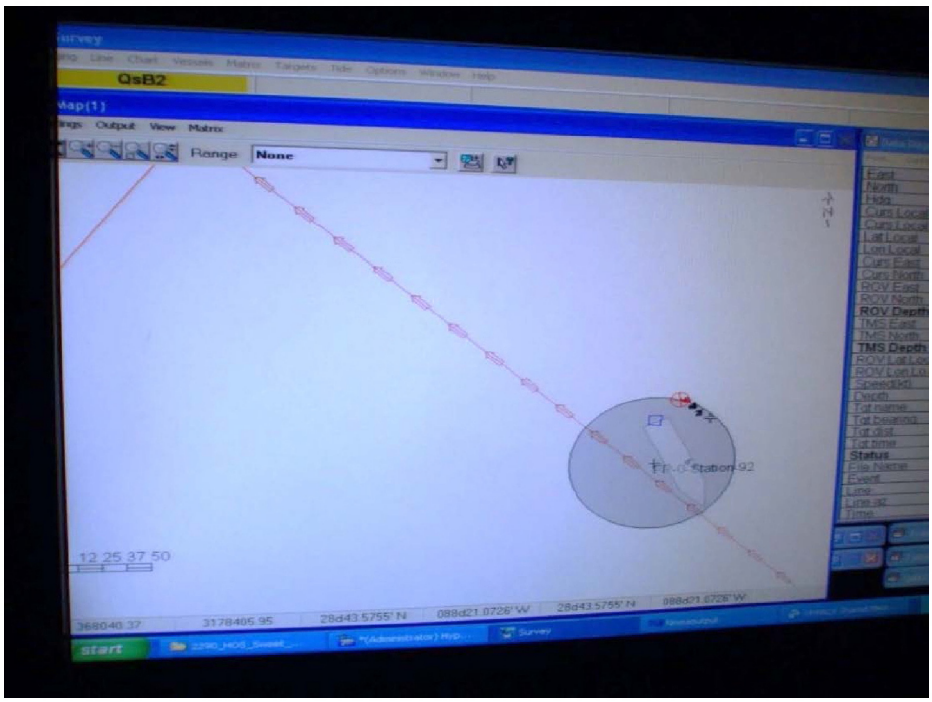


Figure 37. HYPACK navigation display of ROV location relative to the ship and the planned transect with an overlay of the station location (FP-0 Station 92) shown in the gray circle. This display was simultaneously projected in the ROV trailer, the science trailer, and the bridge during all ROV operations along each transect. Planned transect direction shown by red arrows.

Figure 38. Bottom ball-valves of GoFlo bottles mounted on the back of the TMS. Undisturbed bottom sediments could be observed ~1/2 m below the bottles.

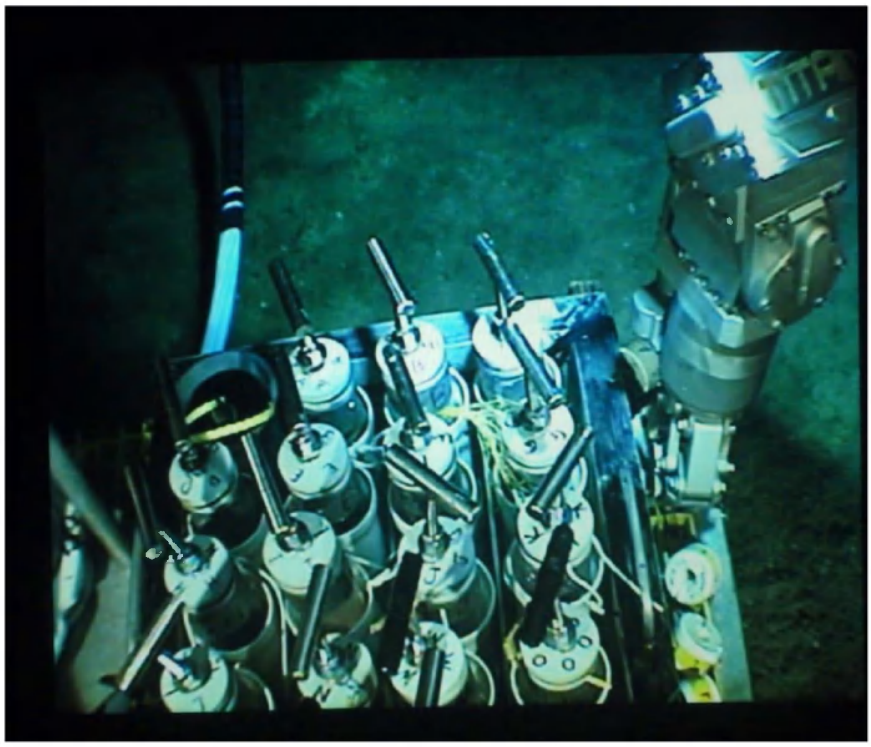


Figure 39. Using the ROV manipulator arm to close a GoFlo bottle by pulling a numbered float (to the right of the push-core rack) attached to a tether line running to the tripping mechanism on a specific bottle.

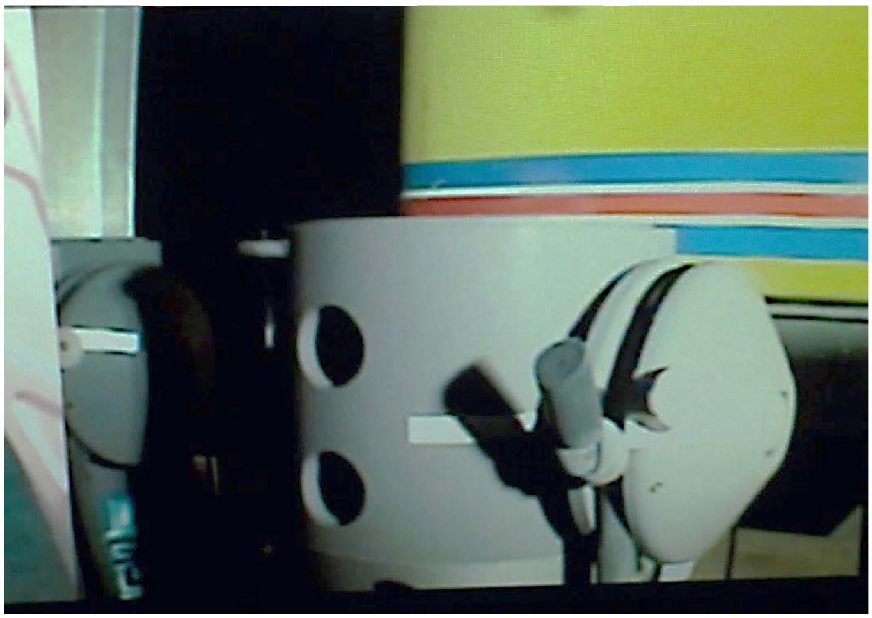


Figure 40. Upper ball-valves of GoFlo bottles mounted on the back of the TMS. The ball valves were closed when the white tape on the pulley lined up with the tape on the bottle.

After the near-bottom water samples were collected, the ROV/ TMS package was usually flown a few meters forward, and the slurp gun prepared for sampling by first removing the slurp-gun nozzle from its holster (Figure 41), and holding it up in clear seawater 2 meters above the bottom while drawing water through the open chamber to thoroughly rinse the sampling tube and nozzle (Figure 42). After flushing, the slurp-gun carrousel was rotated to bring the desired canister into position, and the filter "seated" by drawing a small amount of clean seawater through it (Figure 43). The slurp-gun nozzle was then carefully manipulated to be drawn tangentially across and just above the sediment/water interface (Figure 44) to suction up the loose flocculent material and trap it in the canister (Figure 45). Usually, this operation only took 30-45 seconds, as the very fine flocculent material tended to plug the filters very quickly. After the floc sampling was completed, the suction pump was turned off and the carrousel was rotated again to bring the open/rinse cylinder back into position. The suction pump was then turned back on to rinse the sampling tube, and the collection wand was placed back into its holster.

Following these activities, the ROV/TMS assembly was flown a few more meters along the transect, and the sediment push cores were removed one at a time for triplicate sediment sample collections (Figure 46, Figure 47, and Figure 48). To improve visibility from significant clouds of fine sedimentary material generated during coring operations (and to ensure that a clean, undisturbed sample was obtained by not coring where a sample had already been collected), the ROV/TMS was always flown a few meters up transect between sediment coring events.

At the conclusion of a pre-selected near-bottom water, floc, and sediment sampling station, the *HOS Sweet Water* was instructed to begin moving up the transect again at ~0.5-1 knots towards the next station, and the ROV/TMS was again flown along the transect at 0.5-1 m above the bottom. While in this mode, another empty push core barrel was removed from its quiver in the core-barrel rack, and it was held by the ROV manipulator arm "at the ready" off to the side of the ROV/TMS. The core barrel was held facing up in clear water out of the camera view so as not to restrict our forward visibility, but it could be readily moved into position if necessary for rapid deployment. In this manner, it was possible to sometimes execute what we euphemistically called a "drive-by shooting" wherein a tar ball or clump of oiled sargassum or other target of interest observed in front of the ROV could be "speared" with the core barrel as the ROV/TMS "drifted" over the target 20-30 seconds later. Not all the ROV pilots and manipulator operators had the skill sets to pull this off, but when they did, it was an effective way to collect random samples of opportunity along the transect without having to stop the ship.

During sample processing back on board the ship (see below), photographs and notes were recorded for each sediment core to document the sediment core quality (e.g., undisturbed surface, limited smearing of sediment layers inside the core barrel, etc.). These observations were later used to help select which cores would be analyzed if, for other reasons, all three replicates were not scheduled for analysis. Depending on the skill of the ROV pilot and manipulator operator, a station could usually be completed in 45 minutes to an hour, but sometimes it took much, much longer. Some longer transects (8-10 km with 4 or 5 preselected stations) could take upwards of 14-16 hours to complete.

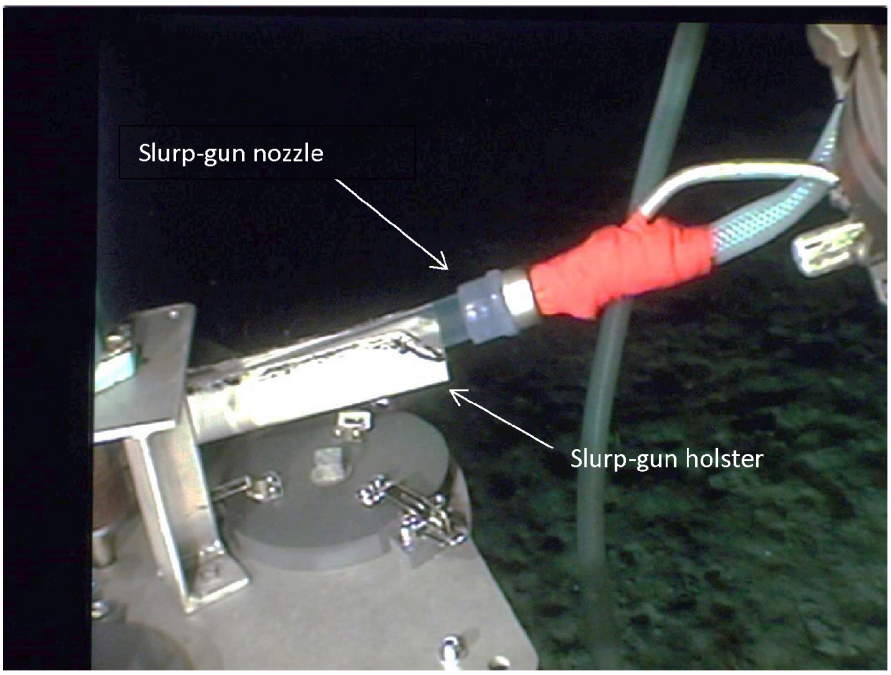


Figure 41 Grabbing the slurp-gun nozzle from its holster on top of the slurp-gun carrousel in preparation for collecting a near-surface sediment floc sample.

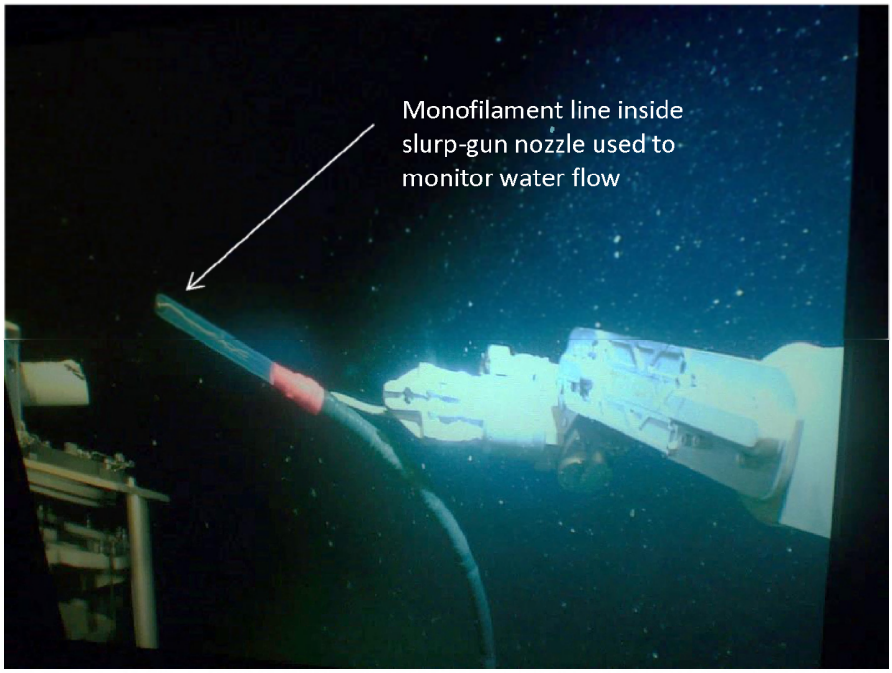


Figure 42 Holding the slurp gun nozzle in clear water to rinse the sampling tube by pulling clean seawater through the open chamber on the slurp-gun carrousel. The yellow monofilament line inside the nozzle was used to visually tell when active suction was being achieved as it would vibrate in the water flow. As the slurp-gun canisters would fill, the water flow would fall off dramatically even though the vacuum pump at the back of the TMS was still running.

Figure 43. Canister ("U") rotated into sampling position in the slurp-gun carousel and its filter "seated" by pulling clean seawater through it before collecting a bottom floc sample. Unused white floc filters are visible in bottom of canisters.

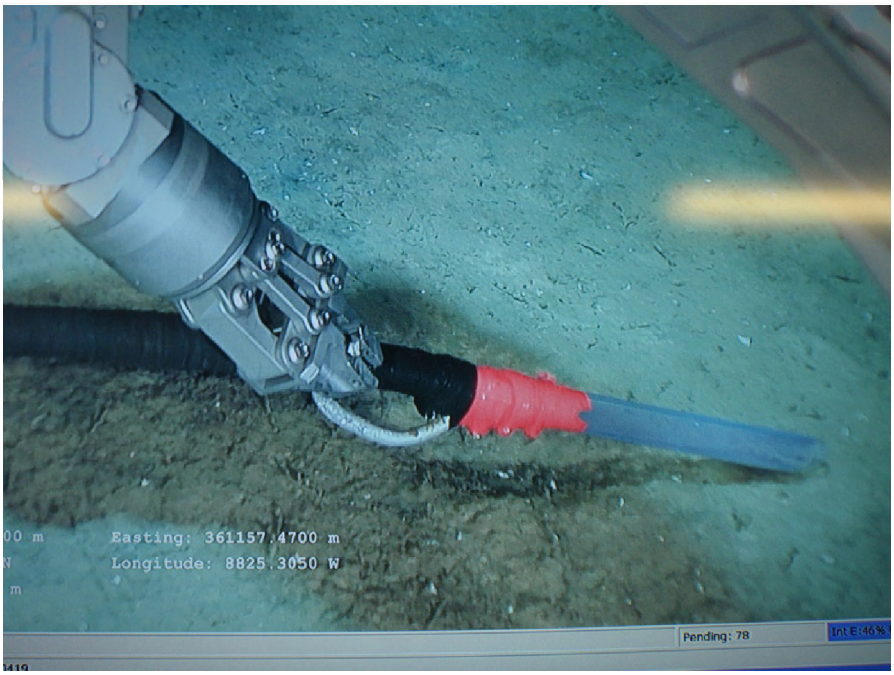


Figure 44. Positioning the slurp-gun nozzle just above the sediment-water interface to vacuum-collect the uppermost few millimeters of flocculent material without disturbing the underlying sediment.

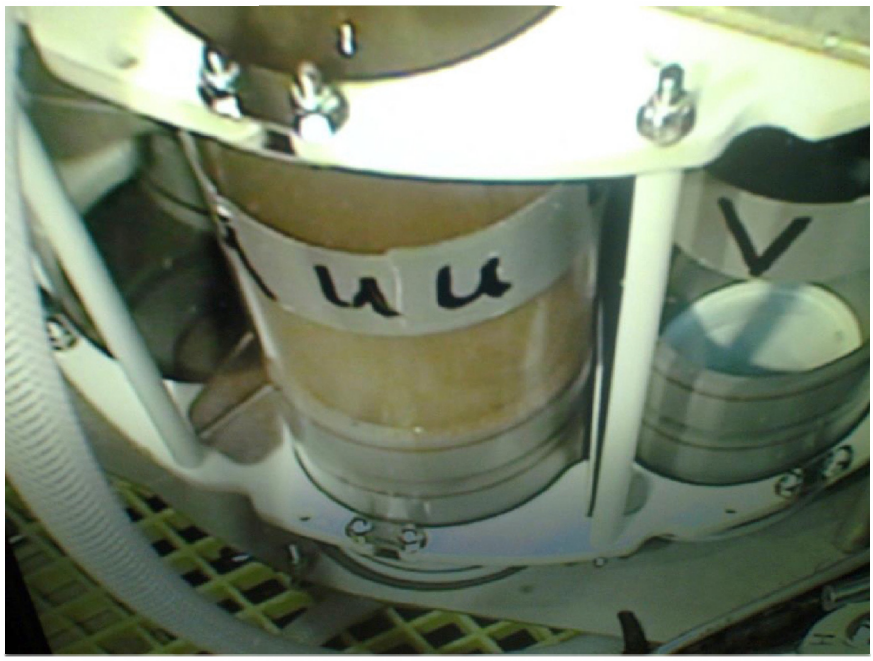


Figure 45. Flocculent material being trapped in slurp-gun canister "U" during near-bottom ROV operations on the *HOS Sweet Water*.

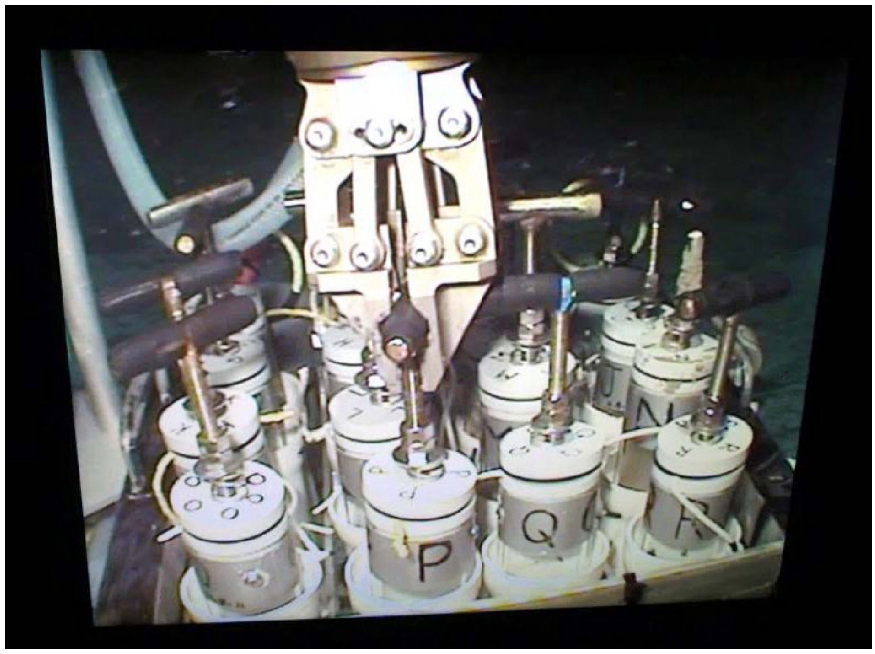


Figure 46 ROV manipulator arm removing a vented sediment push-core from core storage holster in preparation for sediment collection.

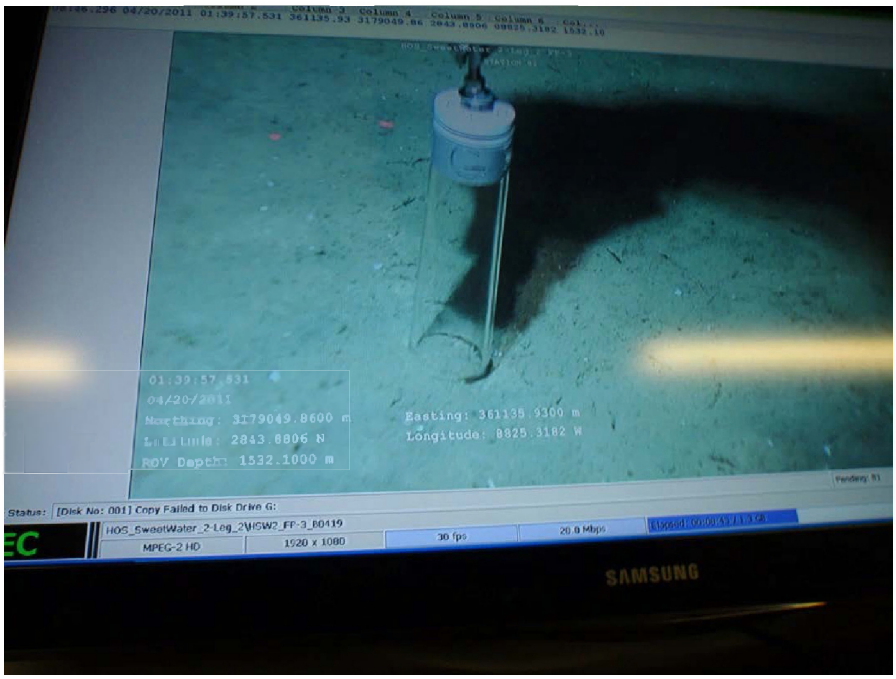


Figure 47. Positioning a vented sediment push core in preparation for undisturbed sediment collection.

Figure 48. Withdrawing the sediment core and showing clean and undisturbed upper sediment surface with little or no disturbed flocculent material in the water above the core.

Sample processing on the HOS Sweet Water

Just as there were protocols for collecting samples along the bottom, there was also a set routine for sample processing in the clean room facility (Figure 49). On deck, the sediment cores were carefully removed from their holsters in the ROV rack and the core's exterior cleaned for photo documentation. If sheen was noted on the supernatant water above the core (Figure 50) or if significant amounts of resuspended sediment were present, it was recorded (e.g. see Figure 34) and the water decanted into a separate container for analysis as a core-barrel sheen or floc sample (Figure 51). Then, pushing up with a bottom plunger, the top of the sediment was extruded into a 1 cm high, sub-sampling ring held atop the main core tube (Figure 52 and Figure 53). The extruded 1 cm section was sliced free using a 1 mm thick, stainless-steel plate and the sediment placed in a pre-labelled sample jar as the 0-1 cm layer. This process was repeated three more times using 2 cm long sub-sampling rings for the 1-3, 3-5 and 5-7 cm sediment layers.

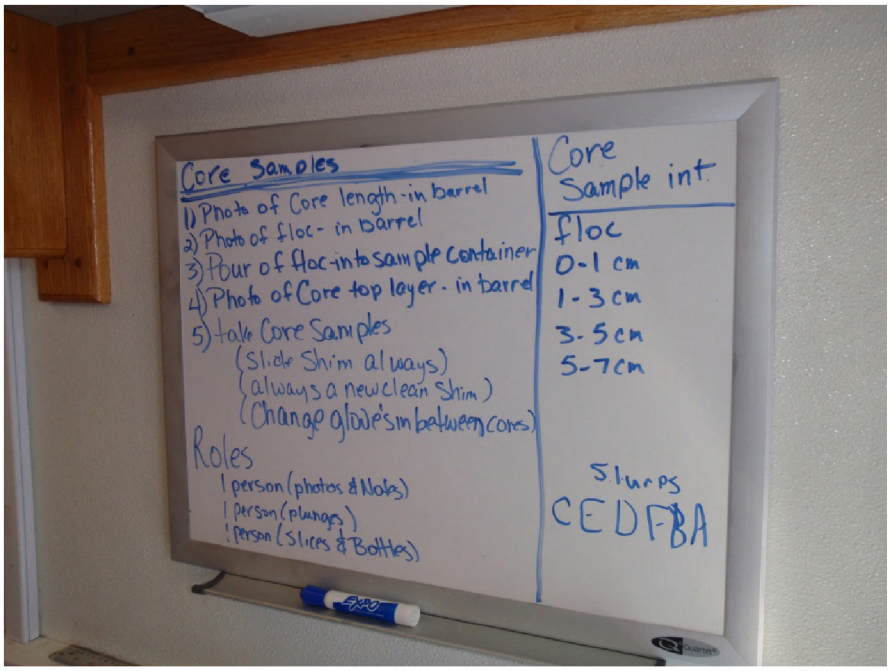


Figure 49 ***HOS Sweet Water*** **clean-room protocol and responsibilities for working up sediment core samples and slurp-gun filters.**

Figure 50. Sheen observed on supernatant water above a push-core sediment sample.

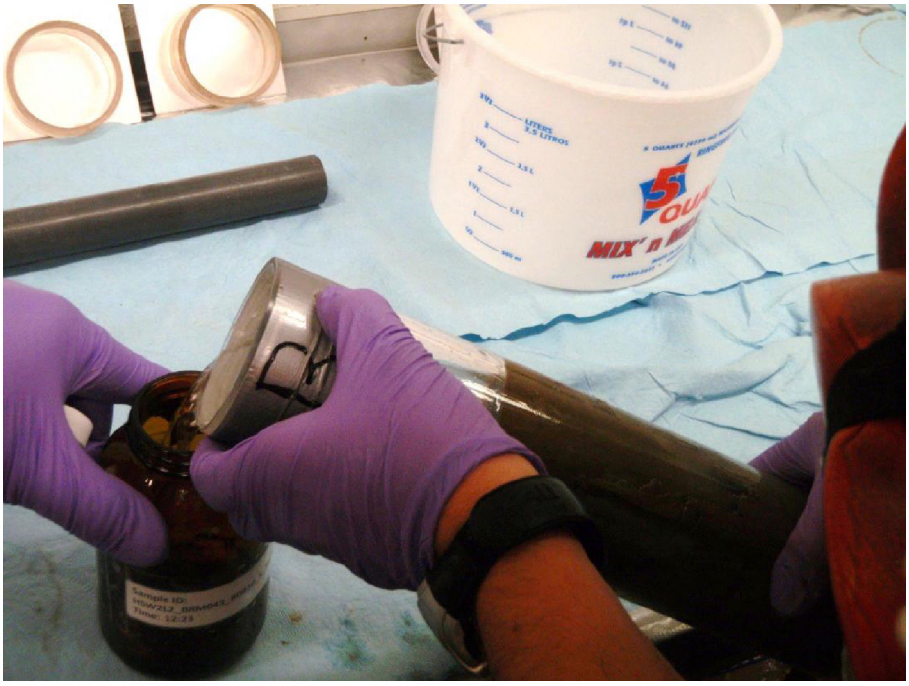


Figure 51. Decanting supernatant water and sheen observed above a sediment core.

Figure 52. Extruding a sediment core from below in preparation for sampling the 0-1 cm layer.

Figure 53. Positioning a 1 cm long core-barrel ring above the sample in preparation for collecting the 0-1 cm layer. After the sediment was pushed up with a plunger at the base of the core barrel into the 1 cm collection ring, a 1 mm thick stainless steel plate was inserted between the 1 cm collection ring and the main core barrel thereby isolating the upper 0-1 cm layer. This process was then repeated three more times with a 2 cm collection rings for the 1-3 cm, 3-5 cm and 5-7 cm sediment sections.

Concurrent with the sediment-sample workup being completed in the clean room, the 10L GoFlo bottles on the back of the TMs were sampled (Figure 54). First, two 40 mL aliquots for VOA analysis were removed, and then separate 1 L bottles were drained for Entrix/BP sample splits and NOAA duplicates if desired (Figure 55). These splits also included samples for total suspended solids (TSS), dispersants, and toxicity if requested. Finally, the remaining volume in the GoFlo bottle was calculated, and a measured sacrificial aliquot was removed such that only the upper 3.5 L (containing any potential oil meniscus that might have formed – see section on FBOBs) remained in the bottle. The transfer tubing for the PLVWSS (or Payne filtration system) was then attached (Figure 56), and the remaining volume in the GoFlo bottle was vacuum filtered through the PLVWSS for separation of the particulate/oil and dissolved phases (Figure 57) The particulate/oil phase trapped on the 0.7 µm glass fiber filter (Figure 58) was stored frozen, and the dissolved phase in the 3.8 L amber glass jug housed in the PLVWSS pump box was left in the jug and refrigerated at 2°C.

Figure 54. As the sediment core barrels were being worked up inside the clean-room, the water samples in the 10 L GoFlo bottles mounted on the back of the TMS were processed next.

Figure 55. Aliquots were removed first for VOA analyses (2 x 40 mL) followed by 1 L whole water grabs for Entrix sample splits, duplicates, and total dissolved solids (TDS) analyses. A calculated and measured volume of additional water was then removed to ensure that the top 3.5 L contained in the GoFlo bottle was what was actually filtered when processed with the Portable Large Volume Water Sampling System (PLVWSS). See Figure 56, Figure 57, and Figure 58 and the section on issues associated from sampling From the Bottom of the Bottle (FBOBs).

Figure 56. Preparing to connect transfer tubing from the bottom sampling valve of a GoFlo bottle to the filter unit of the Portable Large Volume Water Sampling System (PLVWSS) also known as the Payne filtration apparatus.

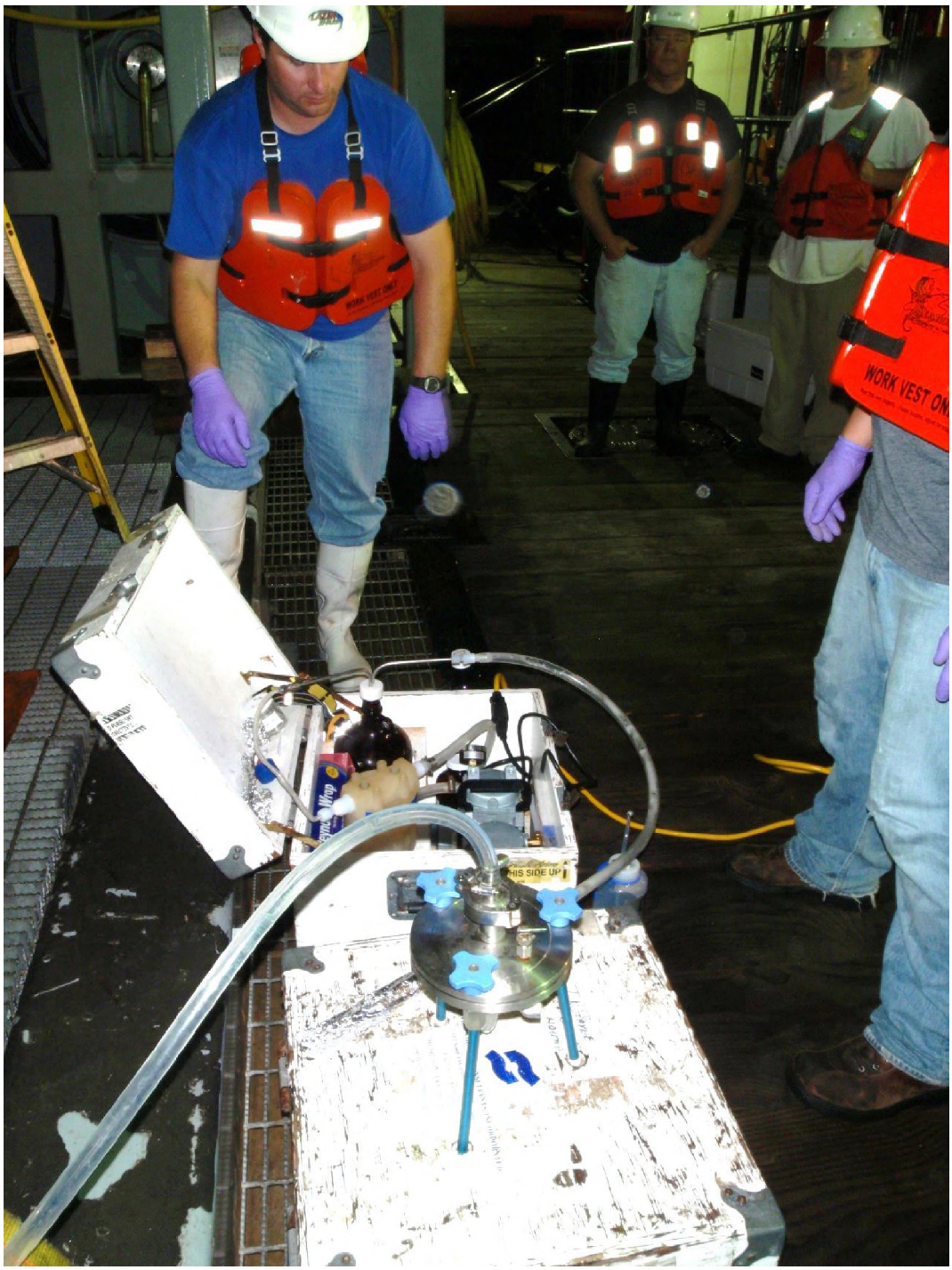


Figure 57. PLVWSS vacuum filtering the last 3.5 L from a GoFlo bottle to separate the particulate oil droplet phase from the dissolved phase constituents that are contained in the 3.8 L amber glass jug held in the pump box.

Figure 58. Particulate phase oil captured on 0.7 µm glass fiber filter in the PLVWSS. After collection, the filters were frozen and the dissolved phase contained in the amber glass jug was stored at 2°C.

After the sediment and water samples were successfully processed, the slurp-gun canisters were removed from the carrousel on the front of the ROV, and they were processed in the clean room. First, the supernatant was examined for any visible sheen (Figure 59), and it was decanted into a labelled sample jar. Then the cylinder barrel was removed from the PVC filter-holder assembly, and the flocculent material trapped on the glass-fiber filter (Figure 60) was photographed and placed in a pre-labelled sample jar and frozen.

Figure 59. Sheen observed on supernatant water above the filter in a Slurp-Gun canister.

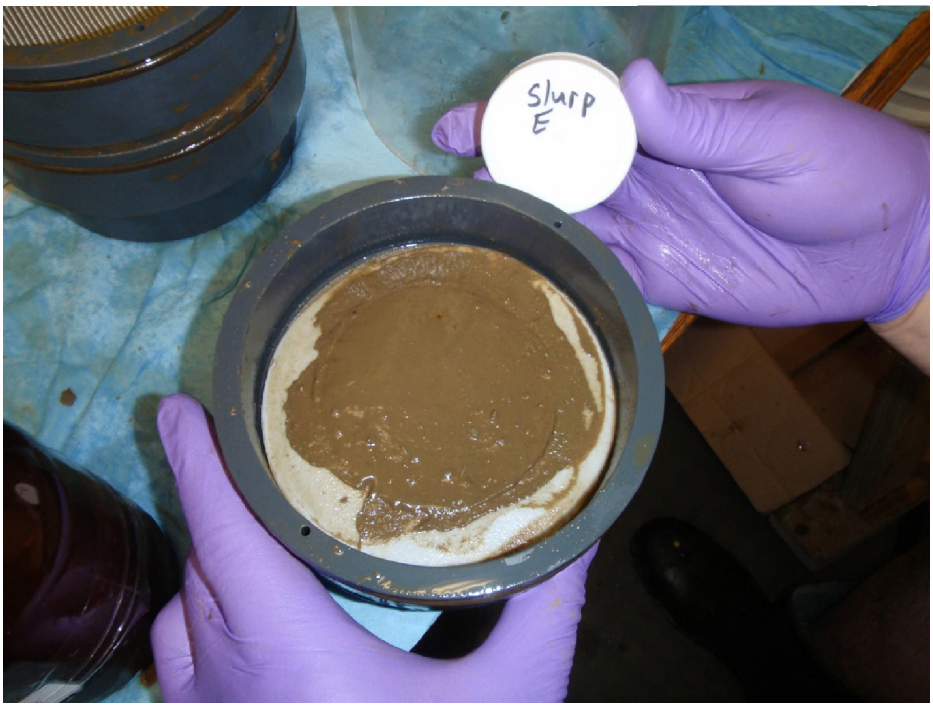


Figure 60 Flocculent material isolated on the glass fiber filter from the bottom of a slurp-gun canister.

With 5-7 dedicated sample processing personnel and 4-5 data managers, it was generally possible to work up all the samples and record the data from a completed transect (~18 sediment cores, 6 GoFlo bottles, and 6 slurp-gun filters) in 2-3 hours. During this interval, the *HOS Sweet Water* was directed to the coordinates for the head of the next transect, and sampling equipment was cleaned, decontaminated, and reassembled. During each cruise leg, this process was repeated on a 24/7 basis for two-to-three weeks, and in this manner the transects and samples shown in Figure 34 were successfully collected during five separate *HOS Sweet Water* cruise legs completed between March and November 2011. The only breaks during any given cruise occurred with ROV or other equipment breakdowns and during sample transfers to the runner boats, but those activities were also very labor intensive (particularly for ROV personnel and the data managers and sample handlers).

Samples of opportunity

The ROV sediment samplers also proved versatile in collecting samples of special interest that were not otherwise amenable for more conventional approaches. One such case was removing flocculent material that had settled on top of a rock outcropping near a suspected seep site on the west flank of Gloria Dome (Figure 61). In this instance, it wasn't possible to obtain a sediment core sample but it was possible to collect the floc material as a slurp sample.

Figure 61. Using the slurp-gun wand to isolate flocculent material settled on top of a rocky outcrop near a suspected seep site.

As noted above, another innovation was to hold a core barrel at the ready during the thousands of meters of transects flown one-half meter above the bottom. Then, when a sample of interest was spotted, the core barrel could be quickly maneuvered to capture samples of opportunity (e.g., burn residues, oil globs, oiled sargassum, or seep samples) as they were encountered on the cruise. In one instance, a small tar lump (suspected burn residue), too small to be retrieved by the articulating arm of the ROV, was successfully captured as a "drive-by" sediment grab using an extra core barrel (Figure 62 and Figure 63) without having to stop the ship.

Often, when hard or semi-solid materials were captured with core tubes, the target material was displaced to the middle of the sediment during core penetration. This obviously messed up the sediment layers, but in such instances, the tar-ball or hard material was the objective. Later, when the sample was retrieved back in the clean room on the ship, the surrounding sediment was easily washed away yielding the intact sample (Figure 64 and Figure 65).

In other instances, some oil residues were very small or so thin that they could have been compromised or possibly lost if a push-core were used for their collection. When these were spotted, it was more appropriate to notify the bridge and ask them to stop the ship and go on DP so that the slurp-gun could be used to capture the samples of interest (Figure 66). Later, during the canister processing, the flake of burn residue could be collected intact from the canister filter (Figure 67). These random tar residue and flake samples were later identified as MC252 burn residue (Stout and Payne 2015), and along with other samples such as oiled sargassum that were also collected from the bottom, they confirmed another mechanism for transporting surface oil to the benthos.

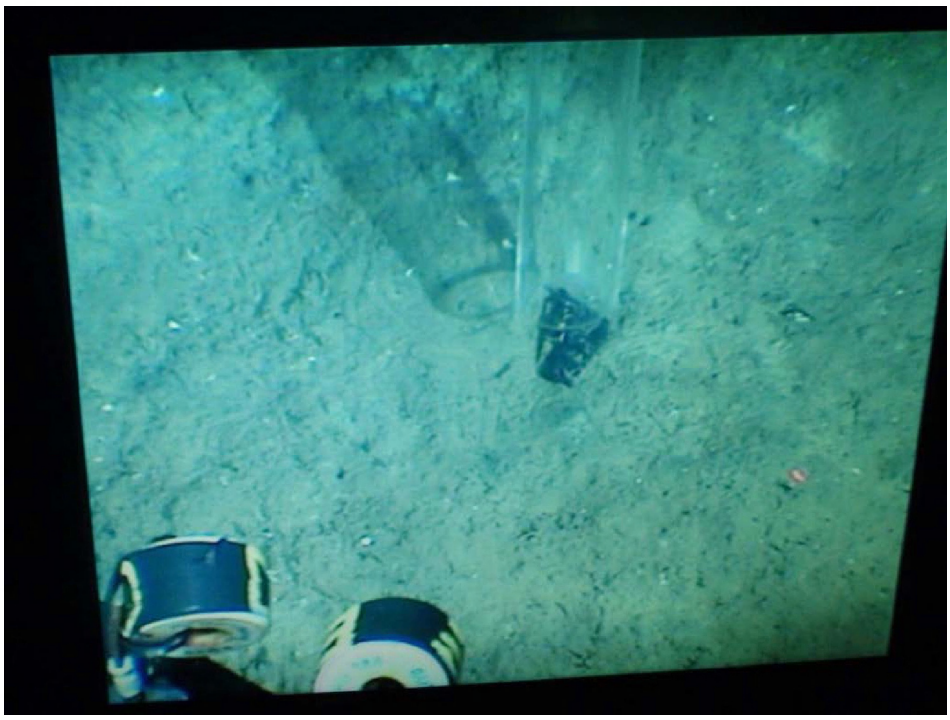


Figure 62. Screen grab of the video display showing the core barrel over a tar lump just before penetration. Note the core-barrel shadow showing the core barrel is still several cm above the sediment.

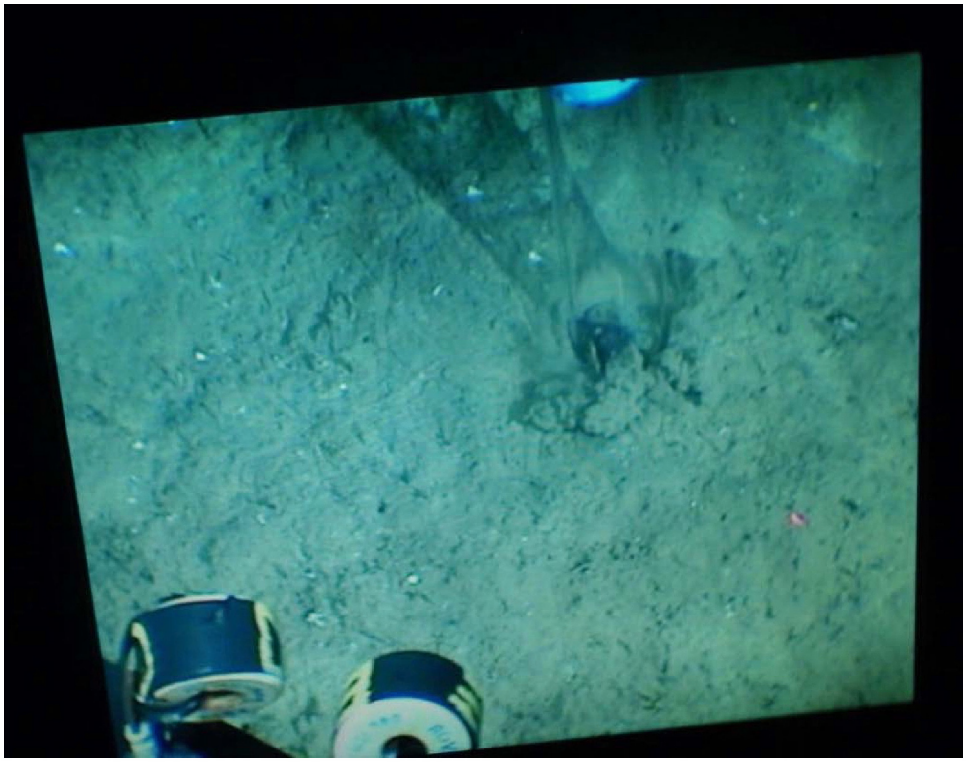


Figure 63 Core barrel D penetrating the sediment with the tar lump still showing inside the barrel.

Figure 64 Extruded core and removal of the tar lump with forceps from the center of the core.

Quality Control

Contaminants—ROV maintenance

The list of potential oil-based contaminants aboard a vessel is intimidating: fuels, lubricants, anti-corrosion products, hydraulic fluids, engine or generator exhausts, bilge discharge, suntan lotion, cigarette smoke, etc. The prevention is, of course, adequate decontamination procedures—and vigilance. It is not difficult to clean a sampling device of oil residues using appropriate detergents but keeping it clean until it gets beneath the water surface is where meticulous vigilance is required. Both during deployment and sample processing, coordination with the bridge is required to keep exhausts moving to the side (abeam of the ship) or downwind of the deployment, retrieval and processing areas. Likewise, portable generators powering winches or deck lab facilities may need to be relocated, and cigarette smoking should be limited to downwind areas. If the sampling crew is cognizant of contamination issues, most risks can be controlled procedurally (e.g., frequent changing of gloves, checking wind direction, sight-and-smell checks for exhausts, and setting up dedicated clean-rooms for sample processing). With each subsequent DWH cruise, more sophisticated and adaptive sample-handling protocols and facilities were established but in the end, it was also prudent to do a bit of onboard precautionary sampling; for example, taking a sample of the deployment crane's or ROV's hydraulic fluids, ships fuels (bunker and diesel oil for generators), and lubricants, etc. that may help de-confound or at least explain some otherwise perplexing samples appearing during data analysis.

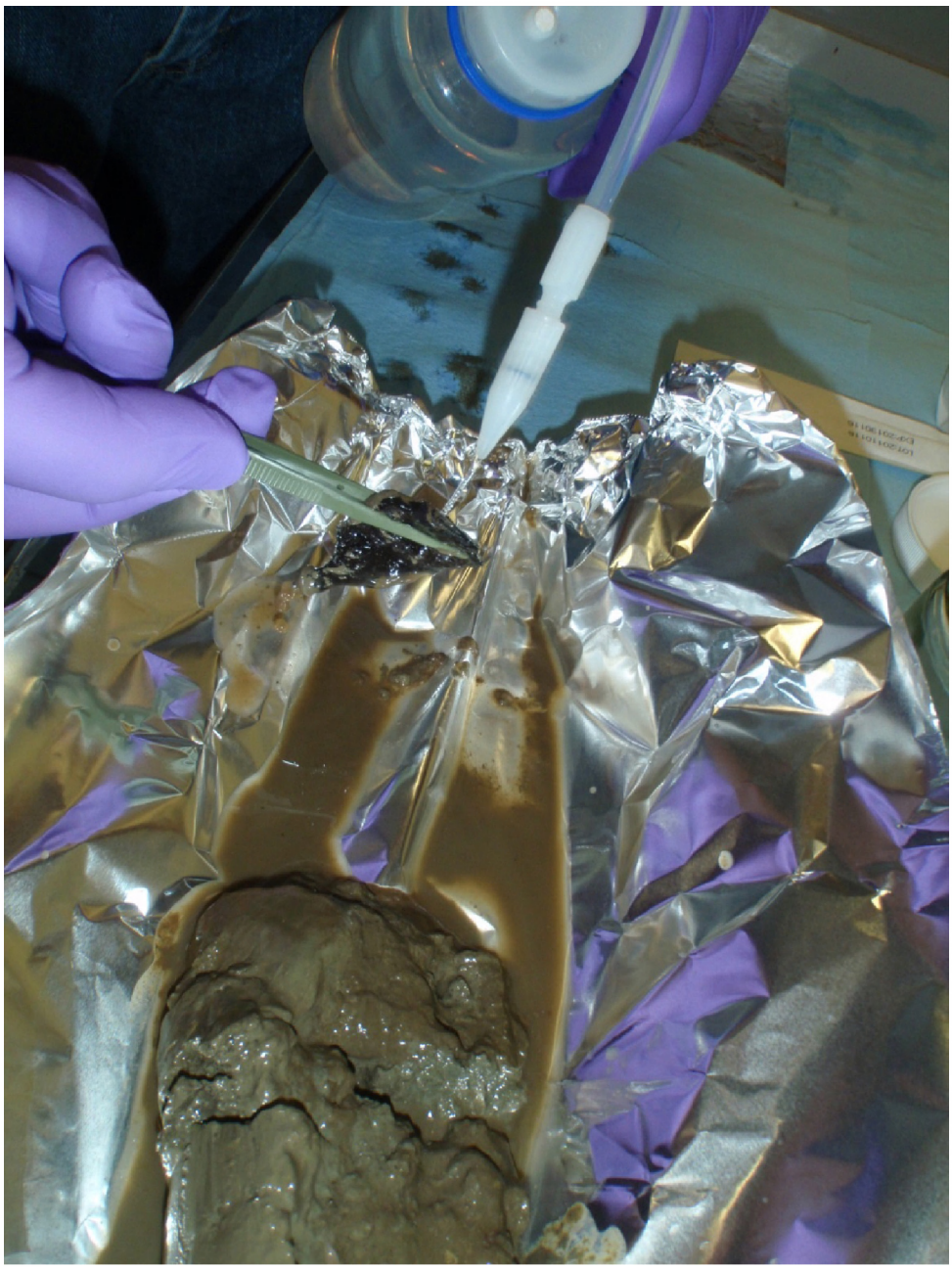


Figure 65. Isolation of a burn residue sample from the sediment by-catch also collected in the core sample. This sample was later identified as MC252 surface burn residue (Stout and Payne 2015). .

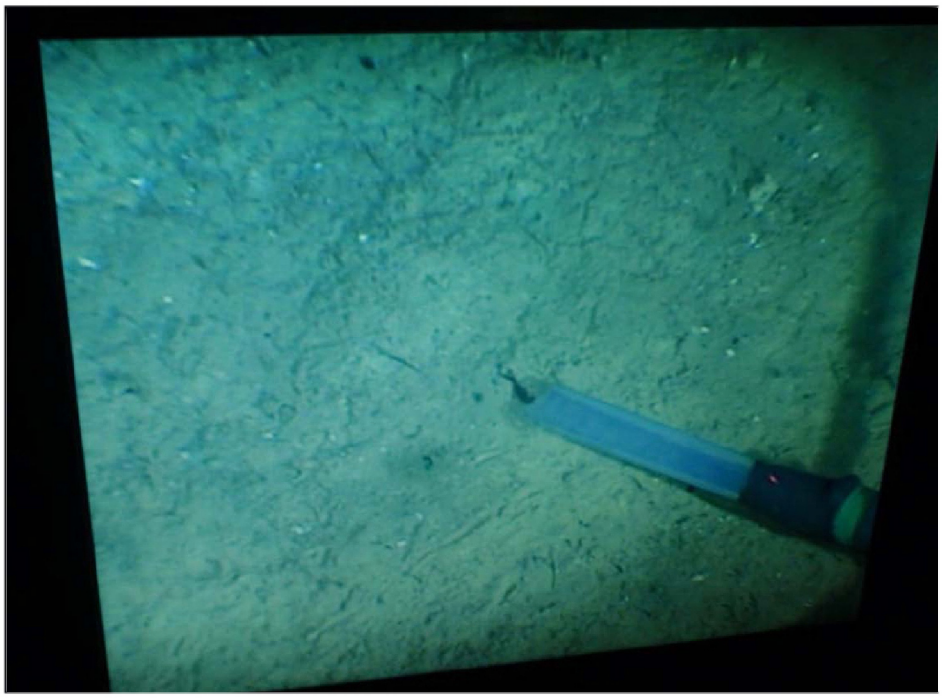


Figure 66. Using the slurp gun vacuum system to collect a flake of burn residue from the bottom.

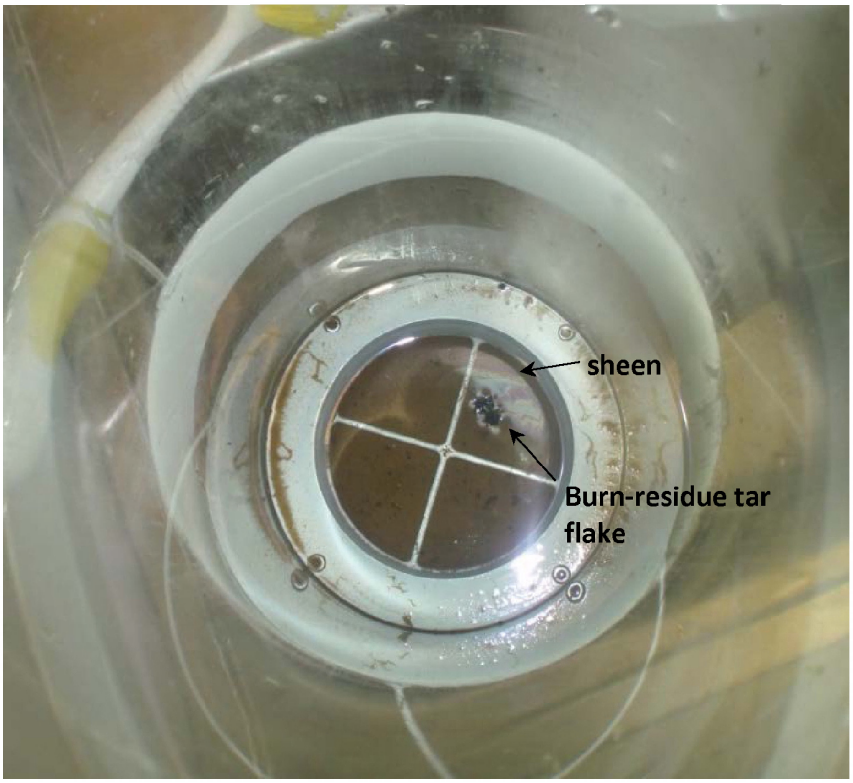


Figure 67 Filter trap at the bottom of Canister B showing the captured oil/tar flake emitting a sheen. This sample was later identified as MC252 surface burn residue (Stout and Payne 2015).

As useful as the ROVs were in visualizing and sampling the submerged oil plume and allowing the collection of completely undisturbed sediment and floc samples, they also compromised some samples with inadvertent leaks of hydraulic fluid. Fortunately, this potential issue was first discovered early during the *Jack Fitz* 1 cruise (13 May 2010), and samples of the hydraulic oil used in manipulator arms and pressurized electronics compartments on the ROV and TMS were collected for later use in forensics analysis. Thus, if hydraulic oil was detected in a sample (usually evidenced by high DBT and hopane), its contribution to the TPAH could be estimated. On the *HOS Sweet Water*, one of the hydraulic pistons on the TMS launch and recovery system (LARS) A-Frame developed a leak; prudently obtaining a sample turned out to be invaluable during later sediment sample forensics analysis (Stout, 2015b).

ROVs and their attendant support systems are very complex, and often during the cruises, replacement parts were not available or had to be shipped from Europe. During the DWH event, it was not always possible to return to port for repairs, and given the time pressure to collect thousands of water samples as well as representative and opportunistic sediment and sunken oil samples along literally hundreds of kilometers of near-bottom transects, it was sometimes necessary to make ad-hoc repairs at sea. This was certainly the case with TMS LARS A-Frame, where we were forced to proceed knowing that extreme care would be required to protect any samples from the leaking A-Frame once they were returned to the deck. In such instances, all that can be done is collect samples of the leaking fluids, and hope that any sample contamination can be sorted out during forensic analysis.

Trying to complete sampling for trace-level (ng/L or ng/g) PAH with systems that were basically designed for offshore engineering support activities is always going to be difficult. A minor hydraulic leak is not a problem when you are trying to repair an underwater pipeline or a weld, but it can be a very serious issue for water and sediment sampling at part-per-trillion levels. At several times during the *HOS Davis* and *HOS Sweet Water* cruises, BP held meetings with their ROV sub-contractor teams to insist on better ROV maintenance, but complicated pieces of equipment will break down and accidents can happen.

Field quality control samples

Typically, field samples are both difficult and expensive to obtain, process, and deliver to the lab; even more so for offshore, deep-water samples. However, if the extra time and expense is not expended in the field to maintain adequate assurance of quality control, the integrity of field results is uncontrolled. Sampling duplicates (two separate samples from the same location/depth), field duplicates (two samples from the same Niskin/GoFlo bottle), equipment blanks (rinse water through the Niskin/GoFlo or the pump or filtering gear), and rinse water blanks are all essential to assuring the samples don't include a background artifact.

A forensic analyst's worst case is having a common pattern appear in a set of samples from a depth/site where the pattern shouldn't occur and while suspecting it is a sampling artifact lacking sufficient field QC data to confirm or understand the source of the issue. Such is often the case with field equipment rinsate blanks. Most commercial sources for distilled or deionized (DI) water used for decontamination rinses do not provide water of adequate purity compared to the often pristine, background seawater nor do the suppliers analyze their water to test for background contaminants. It is not uncommon for supplied DI rinse water to be high in naphthalenes or non-trace levels of other PAH and detergent residues. In such instances, the data interpreter can only ignore the rinse blanks, knowing they are false positives unrelated to field results. For this reason, it is desirable for spill responders to pre-identify DI sources and complete pre-deployment (shipment) analyses for contaminants of concern, but this was not possible during the DWH cruises where thousands of gallons of DI water from dozens of suppliers were used. Therefore, for the sake of "precautionary insurance" mentioned above, Chief Scientists were advised to ship an unopened container of field DI water (in the original manufacturer's or supplier's bottle) from the field for lab analysis for comparison to field and equipment blanks.

Sample processing logistics

Logistics are equally daunting for offshore sampling. Storage options are limited to refrigeration for maintaining water samples as freezing expansion usually breaks glass storage jars and jugs. To meet this need during the DWH event, Conex boxes containing chest freezers converted to serve as 2° C refrigerators were secured to the deck of each boat (Figure 68). But because refrigeration is insufficient to completely stop microbial degradation, holding time to extraction/analysis is also limited (Table 1). Short holding-time limits also means that the volume of water samples from a major cruise could easily swamp a lab's logistics to receive and prepare the samples. Therefore, every effort was made during the DWH event to optimize delivery to the lab, including transferring samples in the field mid-cruise from the sampling platform to a runner boat (Figure 69 and Figure 70), and having a designated logistics outfit to streamline packing coolers, perform forms checking, and expedite and coordinate chilled overnight shipments to the labs. Custom records-management software was designed to produce COCs and fill in sample-log databases. The labs were alerted to impending shipments (including Saturday deliveries) for them to stock supplies and schedule staffing to receive and extract samples. For the DWH event, only 217 of 22,039 water samples (0.98%) were compromised by exceeding the AQAP 14-day maximum hold time.

Table 1. Water Holding Times (adapted from *Deepwater Horizon* NRDA Analytical Quality Assurance Plan (AQAP, 2014)

Matrix/Analysis	Storage for Samples	Holding Time to Extraction	Holding Time to Analysis
VOC Analyses			
Water	Refrigeration 4ºC ±2º with no headspace; Optional: Preserved with HCl in the field in VOA vial.	Not applicable	7 days if not acid preserved; 14 days if acid preserved
PAH, SHC/TEH, Biomarker Analyses			
Water	Refrigeration 4ºC ±2º; Optional: Preserved with 1:1 HCl to pH<2	7 days if not acid preserved; 14 days if acid preserved	40 days from extraction;* except biomarkers no holding time
Filters	Frozen (-20ºC ±10ºC)	4 Years	40 days from extraction;* except biomarkers no holding time
Dispersants (DOSS) Analyses			
Water	Frozen (-20º ±10ºC), 15mL plastic centrifuge tubes	Not established	Not established
Metals Analyses			
Water	Preserve with HNO_3 to pH <2	Not applicable	6 months except Mercury: 28 days

*40 days is an advisory extract holding time. Extracts should be held at -20C in the dark, and may be analyzed past 40 days and results not qualified if surrogates are within criteria.

At the start of the DWH event, the EPA suggested hold time for non-water matrices PAH samples was 1 year. Recent limited lab trials by the DWH NOAA NRDA chemistry team in cooperation with BP have demonstrated excellent analytic stability for unprocessed sediment and tissue samples when stored at -20° C for up to four years (Baker et al. 2014). Analytic trials for frozen, four-year-old stored sample extracts (not matrix specific) also showed excellent stability (Alpha Analytical Laboratory unpublished data 2015). The DWH AQAP reflects these sample stability findings (Table 2).

Table 2. Sediment Holding Times (adapted from *Deepwater Horizon* NRDA Analytical Quality Assurance Plan (AQAP, 2014)

Matrix/Analysis	Storage for Samples	Holding Time to Extraction	Holding Time to Analysis
VOC Analyses			
Sediment	Refrigeration 4ºC ±2º For preservation requirements, see SW-846 Method 5035A.	Not applicable	14 days
PAH, SHC/TEH, Biomarker Analyses			
Sediment/Soil (also total solids, grain size and TOC)	Frozen (-20ºC ±10ºC), except Grain Size should not be frozen – store at 4ºC ±2º	4 Years, except not applicable for Grain Size, Total Solids, and TOC	40 days from extraction[14]; except biomarkers grain size, total solids and TOC no holding time.
Dispersants (DOSS) Analyses			
Sediment and Tissue	Frozen (-20º ±10ºC), glass jars	Not established	Not established
PCB Congener Analyses			
Sediment and Tissue	Frozen (-20º ±10ºC)	4 Years	40 days from extraction[14]
Metals Analyses			
Sediment and Tissue	Frozen (-20°C ±10°C)	Not applicable	2 years except Mercury: 1 year

Figure 68 Aft deck of the *HOS Sweet Water* showing Conex container housing chest-freezers converted to 2° C refrigerators (right under light), the TMS umbilical cable winch (left foreground), the generator for the TMS/ROV (yellow), and other assorted containers for expendable supplies.

Figure 69 Runner/supply-boat preparing for stern-to-stern transfer of frozen and refrigerated samples to be ferried under temperature-controlled conditions into port for coordinated overnight shipment to the laboratory.

Figure 70 More typical, side-to-side transfer of samples to a runner boat (with refrigerated and freezer containers) for later overnight-shipment to the receiving laboratory.

Conclusions

Sampling the deep ocean for oil hydrocarbons is a challenging and technically demanding task with multiple opportunities to get it wrong—which won't be known until the data come back from the lab. But if done properly, the resulting data can be highly insightful in understanding the weathering, fate, and transport of spilled oil.

During the *Deepwater Horizon* event, adaptive sampling was successful in developing and using a package of sensor and sampling gear assembled on a rosette platform to track the deep subsurface plume. Further improvements to the package incorporating video and droplet-size measuring cameras as it transferred to the ROV platform greatly enhanced the ability to capture relevant samples and make observations regarding the oil behavior in the deep ocean. The ROV platform also proved invaluable for sampling near-bottom water samples and identifying and collecting floc samples, burn residues, and sediments without disturbing the ephemeral oil layer at the sediment-water interface.

Field logistics and laboratory coordination efforts evolved allowing runner boats to pick up samples during extended offshore cruises, and during the year-and-a-half of sampling efforts after the *Deepwater Horizon* event, only 217 of 22,039 water samples (0.98%) were compromised by exceeding the AQAP 14-day maximum hold time.

Acknowledgements

Many dozens of individuals and institutions were involved in the joint NOAA/BP cooperative cruises, and while all those contributing to the NRDA effort cannot be listed, we would like to acknowledge a number of individuals whose contributions were particularly significant while apologizing for others we inadvertently omitted. Dr. Debbie French-McCay, Eileen Graham, Dr. Yong Kim, and Dr. Matt Horn of Applied Science Associates (ASA) are thanked for their tireless efforts in preparing the NOAA/NRDA cruise plans and real-time support with ADCP data analysis and deep plume trajectory modeling. Dr. David Valentine of UC Santa Barbara is acknowledged for assistance with *HOS Sweet Water* cruise plan preparations and for serving as Chief Scientist on the *HOS Davis 5* and *HOS Sweet Water 2 Leg 1* and *HOS Sweet Water 4* cruises. Frank Johnson, Bruce Graham, Terry Stevens, Tony Wadley, Paul Fitzgerald, Mike Dugan, Jeff Riddle, Gray Lawson, Eddie Walsh, Carlos Sardinha, and Gina Brewer of Continental Shelf Associates (CSA); Mark Russo, Paul Sanacone, Sandy Skeeters, Mike Hill, Jim Convery, Jason Land, and Dave Cowart of Mako Technologies (ROV operations); Dr. Cable Davis and Nick Lomas (holographic camera operations), Robert Nelson, Sean Silva, and Dr. Chris Reddy of the Woods Hole Oceanographic Institution (WHOI); and Dr. Mary Woo-Pack (UC Irvine) are thanked for their scientific input, oceanographic skills, and technical support. On-board data management and sampling operations were completed by Brock Sadler, Kevin Cranna, Jason Sadler, Barnaby Friedman, Brad Henrich, Jennifer Aicher, Carla Williams, Brian Camlek, Flynn Daigle, Devon Grimme (Dade Moeller); Mark Krisanda and Hans vanLingen (Coneco); Andrea Quattrini (Temple University); Audra Burchfield, Velu Ochoa, Audrey Jackson (Farson), Dr. Barb Bischof (Dial Cordy); Bo Keopaseut, Laura Rubiano-Gomez, Luke Curci (AIS); Laughlin Siceloff and Jessica Childs (CSS); and Adam Spear (Green Eyes). Dr. Karen Favret, Justin Campbell, Captain Jason Dobbs Lee, Laura Ryckman, Stefan Wodzicki, and Donald Lee of Entrix/Integral are acknowledged for their sampling support and cooperation as BP representatives. Finally, Don Gibson (BP) and the captains and crews on the nine *Jack Fitz*, *HOS Davis*, and *HOS Sweet Water* cruises where Dr. Payne served as Chief Scientist are thanked for their safe operations, vigilance, and 24/7 support during the 2010 and 2011 offshore efforts.

Photo credits: The photographs in Figures 1 and 2 were taken by Eileen Graham or Yong Kim of ASA. The photograph in Figure 12 was taken by Eileen Graham. All others were taken by James R. Payne.

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