

**Water Column Injury Ephemeral Data Collections:  
Cruise 3: Surface Water Sampling Plan for Dispersant Treated Oil  
Deepwater Horizon Oil Spill (DWHOS)  
May 29, 2010**

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Reviewed by: Laura Riege (Entrix) / Robert Mulcahy (CSA)

**Proposed Cruise dates: May 30, 2010 – June 3, 2010**

**Objectives (Tier 1-3 from Ephemeral Data Plan)**

The surface waters (upper mixed layer and potentially other deeper near-surface waters) are and will continue to be exposed to entrained oil droplets and dissolved soluble to semi-soluble hydrocarbons (aromatics primarily) resulting from:

- A. Surfacing oil plumes from deepwater releases and horizontal transport of surfaced oil and the associated oil droplet plume rising from the release sites, with soluble to semi-soluble aromatics already dissolved from the droplets;
- B. Dissolution of aromatics from the surface floating oil (after transport to other areas) into the wave-mixed layer (thickness variable with wave height, about 1m deep)**
- C. Natural entrainment of floating oil (primarily when winds exceed 12 kts) and dissolution of soluble to semi-soluble aromatics into the surface mixed layer (i.e., to 20-40m deep; with more exposure in the upper 1m)**
- D. Chemical dispersant-induced entrainment of oil and dissolution of soluble to semi-soluble aromatics into the surface mixed layer (i.e., to 20-40m deep; with exposure highest in the upper 1m but potentially extending deeper than for natural entrainment)**
- E. Transport of oil droplets and dissolved soluble to semi-soluble aromatics in surface advective flows, including in eddies, along fronts, etc.

The objective of this sampling plan is to address pathways described in B to D above, and particularly D chemical dispersant-induced entrainment of oil and dissolution. More specifically, the objective is to obtain surface and sub-surface water samples for water impacted by oil believed to be from the MS Canyon 252 event for polycyclic aromatic hydrocarbons (PAH's) and total petroleum hydrocarbon (TPH) characterization and TPH fingerprinting. Samples will be collected opportunistically from areas identified by the Special Monitoring of Applied Response Technologies (SMART) teams, or other information sources as being target areas for the application of aerial dispersant. Samples will be collected before and after application of aerial dispersant. For the purposes of this work, sampling locations will be based on United States Coast Guard (USCG) SMART Operations, and will vary according to the abilities of response crews to identify areas suitable for the addition of dispersant. Fingerprinting results from this initial oil sampling effort may be used to validate fate and transport model inputs, particularly concentrations of TPH's at or near sampling locations.

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The cruise will record the physical and chemical conditions of surface waters as follows:

- A. Conductivity, Temperature and Depth (CTD) for characterizing the surface mixed layer and pycnoclines;
- B. CDOM fluorescence for indicating the vertical distribution of hydrocarbons;
- C. Whole water samples for measurement of
  - PAH (complete suite of alkylated PAHs),
  - BTEX,
  - TPH,
  - Dispersant concentrations,
  - Oil droplet size
- D. Surface oil photography and oil samples for weathering analysis;
- E. Oil droplet size distribution using FLOWCAM;
- F. Plankton (zooplankton, including ichthyoplankton, decapods larvae and holoplankton) identification and density counts; percentage alive analysis; using FLOWCAM and ZOOSCAN.

#### **Locations to be sampled:**

This cruise will not be sampling within 5 nautical miles (nm) of the source location. Sampling and physical oceanographic data will be collected at stations located in areas where aerially-applied, or surface-vessel-applied, oil dispersants and untreated oil at various stages of weathering are present. The station locations will be determined based on dispersant operations at the time of the cruise and attempt to characterize these waters before and after dispersant application. We will coordinate with SMART teams to the extent possible. Samples will also be taken at reference locations outside the plume, in clear waters without surface oil while en-route to the area of sampling. We plan 3 days of sampling in the upper mixed-layer above the first pycnocline (approximately 10-15m depth). We estimate ~36 stations will be sampled, with 3 water depths sampled for chemistry per station (total of ~100 discrete water samples).

#### **Methodology:**

##### **1. Physical oceanographic data collection upon arriving at each station (CTD):**

Conductivity Temperature and Depth (CTD) profiles will be acquired to determine water column stratification and other physical oceanographic parameters that will help determine depth of sample collections. The CTD probe will have a dissolved oxygen (DO) sensor and CDOM-measuring fluorometer using a Seabird CTD package. A J-frame or larger, a winch and wire (at least 100ft long

##### **2. Water column sampling and collection:**

Samples will be taken to test for the presence of dispersed oil and droplet sizes. Water samples will be taken with Go-Flo bottles. The samples for dispersant measurements will be collected in 1 L plastic bottles. Droplet size will be determined using FLOWCAM with image analysis.

Water samples will be collected for chemical analysis of: PAHs (complete suite), BTEX, TPH, and dispersant concentrations. Remaining sample water will be saved for other analyses. Whole water samples will be taken in 1L I-Chem Certified Clean amber glass jars. These samples will be analyzed for the full suite of PAHs and/or dispersant indicators along with Total Dissolved Solids (TDS) as desired. Remaining sample water will be saved unfiltered for microscopic and other instrumentation for enumeration of droplet sizes and number density.

Water samples will be collected at three depths: just below the surface, mid mixed-layer (between thermocline/pycnocline and surface) and just below the thermocline. A conventional winch and wire system with Go-Flo bottles will be used to collect the water.

### **3. Surface oil samples for weathering analysis:**

Surface oil samples will be taken and placed in (cleaned) amber 125 mL bottles. Digital photography will be used to document surface oil appearance and thickness. Surface oil samples will be measured for water content (i.e., mousse), PAH content and biomarkers. Surface sheen and very fluid fresh oil samples will be collected with pre-cleaned Teflon nets attached to fishing weights by casting from the leeward side of the vessel with a conventional fishing pole. After the Teflon nets are drug through the sheen, they will be sealed in 125 mL glass jars for shipment to the laboratory. Water content analyses of mousse samples will be completed at the laboratory via Karl Fischer titration. PAH analyses will be completed by selected ion monitoring GC/MS and will include alkylated homologues as well as parent compounds. Biomarkers (steranes and triterpanes) will be completed on oil and other specific samples by selected ion monitoring GC/MS.

### **4. Analysis of Oil Droplet Size and Microplankton Densities:**

Analysis of oil droplet sizes and phyto/micro zooplankton densities will be performed by Dr. Sutor and technical staff of LSU, using a FLOWCAM system LSU has been using for plankton analysis for 3 years. Fresh samples will be evaluated (on deck) with the FlowCAM and preserved samples will be taken to have a larger volume archived (250 mL or more). Up to a 10-minute run on the FlowCAM will be performed with the fresh samples, less time if there are large numbers of particles of interest.

### **5. Analysis of Oil Droplet Size and Mesoplankton Densities:**

Mesoplankton of interest include ichthyoplankton, decapods early life history stages, and other larger invertebrate zooplankton. Because sampling with neuston or plankton nets in oiled water is not possible, alternative sampling will be conducted for quantitative mesoplankton abundance data. Small mesozooplankton will be collected with a pump system. A diaphragm pump will be used to pump water from discrete depths. The pump intake will be attached to the CTD frame and lowered to the desired depth. Water will then be pumped from the intake to the deck of the ship where it will be filtered through a nitex bags with a dual layer of 1 mm and 60 um mesh nitex. The coarser mesh is designed to remove some of the oil from samples taken in oil affected areas. The oil clings to the fibers of the nitex and large portions of it may be removed from samples through coarse filtration (Eileen Graham (ASA), pers. comm.). The small mesozooplankton targeted by the pump sampling will pass through the larger mesh and be trapped on the finer mesh. The nitex sampling bags will be suspended in containers of water



to prevent extrusions and damage of mesozooplankton through the mesh. The plankton will be rinsed off the fine mesh and the coarse mesh will be visually inspected for any larger mesozooplankton that may have been captured and these will be removed with forceps and placed in the sample. The sample will then be preserved in 4% formalin solution and returned to the lab for analysis.

ZOOSCAN analysis of mesozooplankton samples will be carried out in the laboratory. The ZOOSCAN is designed to analyze a preserved mesozooplankton sample, identifying organisms to anatomically-similar groupings. The ZOOSCAN instrument, which is specifically designed to convert preserved plankton samples into a high resolution digital image, will be employed in conjunction with software to create a permanent record of the contents of each sample. Each individual zooplankton sample in the scan is detected and isolated by ZooProcess software in a sequence that produces individual images of each organism along with morphological measurements (length, width, area, perimeter, roundness, and other) and other features, which can be used to assist a computer in sorting the images into taxonomic categories. This analysis will be performed by Dr. Sutor and technical staff of LSU data and, where possible, will be compared with archived SEAMAP program samples analyzed for these organisms.

### **Sampling Procedures**

Stations will be identified to represent areas where dispersants are or will be applied to the water surface (by aerial or boat) and non-dispersant applied areas where oil is present on the water surface. Coordination with SMART teams to identify appropriate locations for sampling will be required.

At each station, a CTD cast will be performed, followed by water sampling with Go-Flo bottles. The time required for sampling, to deploy and recover the sampling package and Go-Flo bottles, is estimated at 1 hour. The FlowCAM work will be done in transit. It is anticipated that 4-6 stations can be covered throughout the course of the day, and 3 days will be spent sampling at sea.

### **NOTE:**

Sample collection methodology, handling, chain of custody and decontamination procedures will follow accepted standards to ensure the highest quality data will be collected. Discrete samples will be tested at an approved lab(s).

### **Limitations:**

The cruise needs to be scheduled such that it is completed by June 3, 2010, as Dr. Sutor has other commitments after that date.

### **Equipment needs:**

1. Boat to accommodate 4 NOAA contractors (1 chief scientist (Malinda Sutor), Sean Sylva, and 2 technical staff from LSU to assist with taking water and oil samples plus QA/QC recording); 2 Entrix employees, and 3 CSA employees. Boat and personnel will be prepared for 4 days of transit time and sampling. Total Scientific crew - 8
2. Sampling deployment gear to sample up to 30 ft nominally.



- Seabird CTD with dissolved oxygen and in situ fluorescence for CDOM.
  - 6 - 10L Go-Flo bottles which can be triggered using a messenger system
  - FLOWCAM (for droplet mid-sized measurements)
3. >200 1L amber glass jars for oil and water samples
  4. >200 Pre-acidified VOAs for BTEX samples (min 72; 144 optimal)
  5. 100 1L acid-cleaned plastic bottles (wide mouth) for dispersant analyses
  6. 14 Jumbo Coolers
  7. 32 4L amber glass jars for toxicity samples

### Personnel

4 NOAA contractors:

Dr. Malinda Sutor, 1 technician and 1 graduate students (LSU)

Scientists: Sean Sylva (WHOI)

2 Entrix employees

3 CSA employees: Juan Levesque, Woody Powell, and Erin Hodel

### Vessel

All operations will be completed on the M/V Bunny Bordelon (150 ft) operated by Bordelon Marine, Port Fouchon, La.

### Estimated Costs\*

Vessel Bunny Bordelon Cruise #3: Estimated Costs for a 3 day mission				
Category	Unit Cost	Units		Total Cost
		Type	Number	
Entrix Mobilization Costs Includes equipment mob, vessel prep, Labor and travel	\$173,000.00	Quantity	1	\$173,000.00
Entrix Vessel Costs (not including fuel / lube)	\$21,000.00	Days	3	\$63,000.00
NOAA Scientific equipment costs	\$4,500.00	Quantity	1	\$4,500.00
LSU/NOAA (Dr. Sutor and 2 Technicians)	\$35,000.00	Quantity	1	\$35,000.00
NOAA Contractor Costs (Sean Sylva)	\$1,800.00	Days	5	\$9,000.00
<b>Estimated Total</b>				<b>\$284,500.00</b>

\*Analytical costs are not included in the above cost estimate.

### Safety Plan

This cruise will not be sampling within 5 nm of the source location. Thus, an industrial hygienist is not required on the cruise. A full operations and safety plan has been prepared for review and approval before any planned operations.

**Analytical Laboratory**

All water chemistry samples will be sent to Alpha Laboratories in Mansfield, MA. All biological analyses will be performed at LSU under the supervision of Dr. Sutor. The RP will take additional unfiltered and toxicity water samples at selected locations. These samples will be sent to a laboratory of their choosing. Entrix will provide all related sampling supplies for their samples.

**Distribution of Laboratory Results**

Each laboratory shall simultaneously deliver raw data, including all necessary metadata, generated as part of this work plan as a Laboratory Analytical Data Package (LADP) to the trustee Data Management Team (DMT), the Louisiana Oil Spill Coordinator's Office (LOSCO) on behalf of the State of Louisiana and to ENTRIX (on behalf of BP). The electronic data deliverable (EDD) spreadsheet with pre-validated analytical results, which is a component of the complete LADP, will also be delivered to the secure FTP drop box maintained by the trustees' Data Management Team (DMT). Any preliminary data distributed to the DMT shall also be distributed to LOSCO and to ENTRIX. Thereafter, the DMT will validate and perform quality assurance/quality control (QA/QC) procedures on the LADP consistent with the authorized Quality Assurance Project Plan, after which time the validated/QA/QC'd data shall be made available to all trustees and ENTRIX. Any questions raised on the validated/QA/QC results shall be handled per the procedures in the Quality Assurance Project Plan and the issue and results shall be distributed to all parties. In the interest of maintaining one consistent data set for use by all parties, only the validated/QA/QC'd data set released by the DMT shall be considered the consensus data set. The LADP shall not be released by the DMT, LOSCO, BP or ENTRIX prior to validation/QA/QC absent a showing of critical operational need. Should any party show a critical operational need for data prior to validation/QA/QC, any released data will be clearly marked "preliminary/unvalidated" and will be made available equally to all trustees and ENTRIX.

**Cruise Chief Scientist and PI:**

Dr. Malinda Sutor Department of Oceanography and Coastal Sciences, Louisiana State University 2179 Energy, Coast, and Environment Bldg., Baton Rouge, LA 70803 Office: 2265 Energy, Coast, and Env. Bldg. (225) 578-8055 office (225) 578-6513 fax (225)241-5224 mobile msutor1@lsu.edu

Bio Dr. Malinda Sutor is a zooplankton ecologist who received her doctorate from the College of Oceanic and Atmospheric Sciences at Oregon State University. She is currently a Research Associate V in the Department of Oceanography and Coastal Sciences (DOCS) at Louisiana State University and holds an appointment as Guest Investigator in the Biology Department at the Woods Hole Oceanographic Institution (WHOI). Her current research includes studies of the fine-scale patchiness of meso- and micro-zooplankton using optical imaging, direct sampling, and glider-borne acoustics. Dr. Sutor has extensive experience processing and identifying meso-zooplankton samples using digital silhouette photography. She conducted plankton sampling and sample analysis while working at the Woods Hole NMFS Laboratory as part of the US GLOBEC Georges Bank program. Dr. Sutor is co-PI of the Southeast Area Monitoring and Assessment Program (SEAMAP), which has been conducting regular plankton sampling at approximately 270 fixed stations throughout Gulf of Mexico (Gulf) within the US Exclusive Economic Zone (EEZ) since 1982.

## Sample Collection Procedure

- 1) Properly trained sampling personnel will perform the sample collection. Trustee and/or RP representatives shall document the sampling, fill out the sample labels, log book, chain of custody forms, sample location and photo-document the sampling.
- 2) Appropriate PPE is to be donned during the sampling event.
- 3) Sample Containers: 1L amber glass containers pre-cleaned and certified with certificate of analysis and bar coded with Teflon line caps required.
- 4) Procedures for taking samples from the surface of the water will vary with the sheen size and thickness, on-scene weather and sea state, the type of petroleum product, and all necessary safety precautions.
- 5) Conduct steps 6-11, inclusive before dispersant application and post dispersant application.
- 6) Collect the surface water by lowering the sample jar into the water and skim the oil layer or globules from the water surface into the sample jar. Continue the process until the sample container is approximately full, making an effort to limit head space. Decant if necessary, repeat until oil collection is complete. If the RP requests, split or duplicate samples will be collected.
- 7) Place the lid firmly and securely on each jar. Wipe any excess oil and water from outside of sample jar using dry cloth or towel. Properly dispose of dry cloth or towels.
- 8) Collect GPS (latitude and longitude) information for each sample.
- 9) Wrap Teflon tape tightly around edge and top of lid to seal the lid onto the jar. Place a custody seal on each bottle. Completely fill out with a Sharpie the sample labels. Samples should be labeled following standard NOAA sampling conventions (i.e., LAAP33-A0523-09901; first six characters are location code, second five characters are date code (where A=2010), "0" is for matrix (oil), 99 is sampling team, 01, 02, 03 is sample number. Place sample jars into original packing boxes.
- 10) Wrap each sample jar in bubble wrap to minimize the chance for breakage and place in coolers on ice to reduce the temperature to 4 degrees C or refrigerate.
- 11) Document sampling date(s), times(s), conditions, volumes, quantities, etc. on Chain of Custody forms. Transfer samples (on ice) to the Houma, LA Command Center for shipment to lab under the supervision of appropriate Trustees and following NRDA sample shipping instructions.
- 12) Sweep surface water reasonably free from oil and collect discrete water samples at 1, 3, and 5 meters using the vessel by spinning the stern into the wind.
- 13) Repeat steps 7-12 inclusive.
- 14) Unless instructed otherwise, Alpha Laboratories will be the receiving laboratory for analytical samples. If RP representatives collect split or duplicate samples, samples will be shipped under separate chain-of-custody. Record the distribution of all samples in a central record in addition to the individual chain-of-custody records.



**Logistics**

- 1) Sampling personnel will travel from Houma to Port Fouchon and board the M/V Bunny Bordelon vessel and will execute the sampling event, then return to Houma. See the attached specifications for the M/V Bunny Bordelon.
- 2) Sampling personnel will transfer the samples and documentation to the Houma Command Center.
- 3) Sampling personnel will prepare the final shipping packages and Chain of Custody documents and associated paperwork, and arrange shipping to the sample recipients.

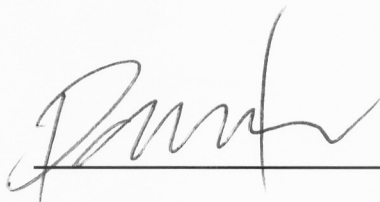
**Attachments:**

Quality Assurance Guidance for Water Column cruise 3 (Dispersant Treated Oil)  
Water Sample Handling Procedures in support of NRDA Cruises  
CSA / Entrix HSE Plan

**Water Column Injury Ephemeral Data Collections:**  
**Cruise 3: Surface Water Sampling Plan for Dispersant Treated Oil**  
**Deepwater Horizon Oil Spill (DWHOS)**  
**May 27, 2010**

**Approvals**

Approval of this work plan is for the purposes of obtaining data for the Natural Resource Damage Assessment. Each party reserves its right to produce its own independent interpretation and analysis of any data collected pursuant to this work plan.



Federal Trustee Representative

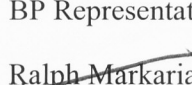

Daniel Hahn (NOAA)

Date

6/5/10



BP Representative

   
~~Ralph Markarian~~ (ENTRIX, Inc.)

Date

June 5, 2010

## Data Quality Assurance Plan for NRDA

### Cruise 3: Surface Water Sampling Plan for Dispersant Treated Oil

#### Purpose

This document provides general guidance for field sampling data quality assurance for the collection of NRDA field samples for planned sampling cruise on May 30 – June 3, 2010 to assist in the validation of

3-dimensional modeling of subsurface plume structure.

The current sampling plan involves sampling 3 depths at numerous stations directed by Dr. D. French-McCay (based on daily overflights and related information) for BTEX, THC, PAHs and free oil droplet size. Sampling requirements as outlined for basic sampling to address field program objectives for adequate description of locations are presented in Table 1. This sampling scheme is derived from the Field Plan and Sampling Protocol documents.

Table 1: Required Analytical Samples for 3-dimensional modeling data support

Sample Type	Volume Needed	Minimum # of samples per location
BTEX	40 mL	2 per depth
THC and PAH	1 L	1 per depth
Oil Droplet and microplankton	variable	1 per depth
Macroplankton	variable	1 per station

In addition to basic site description, additional sampling requirements for data verification and validation, as well as equipment and procedural validation are required. These samples and the suggested frequency are described below.

#### Laboratory Notebook

All errata and observations that do not have a logical spot on the Chain of Custody form shall be documented in a bound lab notebook with numbered pages. Additional notation shall be written in black or blue ink. Entry errors shall be crossed out with a single line, initialed, and dated.

#### Blank Samples

Laboratory Grade de-ionized (DI) water in certified clean glass containers will be provided in order to perform equipment blank analyses. Periodically after decontamination of Niskin bottles, a Niskin bottle will be filled with DI water and left for 10 minutes. Water samples will then be collected in accordance with sample outlined handling procedures. 5 DI water samples shall be collected, where practical, using the laboratory provided water, according to the described methodology for BTEX and THC/PAH analyses (including filtration, where applicable) at each sample location. These samples shall be handled and stored in accordance with the accepted methodology for each sample type.

#### Storage Procedure Monitoring

Aqueous samples shall be refrigerated to 4 °C (+/- 0.5 °C). DO NOT FREEZE. Refrigeration temperature shall be recorded when samples are stored, and periodically monitored and recorded to ensure proper refrigeration. A thermometer will be available to remain with the aqueous samples in storage for monitoring purposes.

#### Methods for sample replicates/splits

To accomplish sample splits, two methods can be employed during the cruise. Method One will be simultaneous deployment of two Go-Flow or Niskin bottles which will be closed at the same depth in order to collect sample water as similar as practical. Method Two involves collecting samples in series from the same bottle upon retrieval. Method One will be the preferred method.



Notation on the sample collection data sheets shall be made. Where messenger assemblies are employed to trigger Niskin bottles, Method Two is the practical options.

#### **Sampling Equipment Monitoring**

All tubing and shall be visually inspected before sampling. Sampling tubing shall be changed when contamination is visually obvious. Tubing changes shall be documented in a separate laboratory notebook (date, time, location).

#### **Sample Depth Determination and Verification**

Where practical, sample depths shall be chosen to best elucidate modeling data needs. For all samples depths must be preset and the depth selections recorded. Verification of triggering sequence of the CTD shall be made and documented in order to verify samples were collected as expected. Niskin bottles shall be numbered and numbers documented with sample station and on Chain of Custody forms. Any malfunction of the triggering of the Niskin bottle operation shall be documented.

## **Water Sampling Protocols in Support of the Ephemera Cruise WATER SAMPLES**

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### Sampling Objectives

- To determine the concentration of oil compounds in the water column.
- To determine the source via fingerprinting, the degree of weathering, and background levels.
- To document exposure of water-column organisms and validate toxicity models.
- To maintain the integrity the sample(s) during sampling, transport, and storage.

### Sample Volume

<i>Analysis</i>	<i>Sample Volume</i>	<i>Reporting Limit</i>
Volatile Aromatic Hydrocarbons (VAH)* by SIM GC/MS (collect in duplicate)	40 mL vials	0.1-1 µg/L (ppb)
Total Hydrocarbon (THC) by GC/FID	1-Liter	15 µg/L (ppb)
PAH (including alkylated PAHs) by SIM GC/MS	1-Liter	0.001 to 0.01 µg/L

\*sometimes referred to as VOA or BTEX analysis

### Sampling Equipment/Containers

- Collect VAH samples (wearing clean Nitrile gloves) by pouring directly from the collection device (4 or 5 L Go-Flow bottle or other sampler) into HCl-persevered 40 mL septum-capped vials. Ensure that there is no headspace (i.e., bubble) in the vial.
- Collect water samples for THC and PAH in glass containers, certified-clean to be organic-free (solvent rinsed). Amber glass is preferred. Leave headspace of about 1 inch for 1 L jars. If the Portable Large Volume Water Sampling System (PLVWSS) is used, the sample will first be processed by vacuum filtration through a 0.7 µm glass fiber filter as it is vacuum transferred from the Go Flow Bottle into the amber glass jug (see separate PLVWSS Protocol).
- If slicks are present, decon samplers before each use (see separate QA Plan for the NRDA Cruise). Wash with laboratory-grade detergent and clean water, with a triple clean-water rinse (distilled water from a local store is OK but laboratory grade, certified-clean DI water is better. If that cannot be obtained, clean “background” water from an up-current non-contaminated area may be used. If sampler is contaminate by an oil slick, an Alkanox wash followed by solvent rinse with isopropanol (or acetone) and methylene chloride is appropriate. If solvents are not available, decontamination with a dilute detergent solution and fresh water, followed by a DI water rinse will be employed, (See separate QA Plan for sampler decon and blank protocol/frequency.) Collect waste solvent rinsate for proper disposal.

### Sample Collection Methods

- Collect subsurface samples below the water surface so as not to include any surface oil.
- Take “near surface” samples from approximately 1 m below the surface as appropriate given weather conditions.
- Boat maneuvers will be performed to attempt to sweep oil away from the area where the Sampling equipment is to be deployed. If Go-Flow bottles are employed, they are to be deployed and retrieved in the closed position. Also applies to sample jars lowered by hand.
- On each cruise, try to sample the control/least oiled areas first, then more contaminated zones.

- Clear surface slicks with a boat hook or pole prior to deploying the equipment, but carefully so that the surface oil is not physically dispersed into the water column. Sweeping the area with sorbents may also be effective.

#### Preservation/Holding Times

- VAH (VOA vial): With no preservative the samples may be held for 7 days at 4°C in the dark. Addition of HCl can extend the holding time to 14 days at 4°C in the dark without loss of sample integrity.
- THC and PAH: No preservative added. Can be held at 4°C in the dark for up to 7 days.
- Immediately place all water samples in cooler and keep at 4°C (do not freeze).
- Use packing material around containers to prevent breakage.
- Ship to the laboratory ASAP with complete COCs. They need at least one day to process prior to holding time expiration.
- **Volatile hydrocarbons** (benzene, toluene, ethylbenzene, and xylene, or BTEX). For oil spill applications, the standard EPA Method 8240 (purge & trap) should be modified by running the GC/MS in selected ion monitoring mode and expanding the scan list (retention times and ions) to include the higher alkylated (C3 and C4) benzenes. Detection limits should be 1 ppb for individual analytes; 0.1 ppb is possible.
- **Total hydrocarbons** (THC). Often referred to as total petroleum hydrocarbons, but most methods do not differentiate among petroleum, petrogenic, and biogenic hydrocarbons. THC by GC-FID (total area of FID gas chromatogram of combined  $f_1$  and  $f_2$  fractions after column chromatography) is often the preferred method because of the low detection limit (compared to other THC methods) and the direct measurement of individual hydrocarbons. This method does not detect low boiling compounds (below  $n\text{-C}_8$ ). For NRDA, THC analyses generally will not provide the data needed to support calculation of toxic effects from PAH exposure, and will have to be corrected to equivalent PAHs. The THC results, however, can be used to track oil weathering and map extent of exposure of water column resources, if meaningful detection limits can be reached. So, get a copy of the GC “trace.” Detection limits are usually higher than those needed for aquatic injury assessment.
- **Polycyclic aromatic hydrocarbons** (PAH). Since most of the toxicity in oil is due to the PAHs, it is often the preferred analysis for NRDA. However, PAHs are expensive and require special laboratory skills. If PAHs are to be measured, it is important that the analytes include the alkyl-substituted PAH homologs, in addition to the standard PAH “priority pollutants.” This method is referred to as Modified EPA Method 8270, because the list of PAHs is expanded to include the alkylated homologs, using GC/MS in the selected ion monitoring (SIM) mode. Detection levels should be 1 ppb for individual PAHs to support injury assessment using toxicity thresholds. Have the lab also run the source oil.

#### Other Considerations

- Contamination by surface slicks is of great concern. Document presence of slicks, weather, wave conditions, etc. which might suggest mixing of surface oil during sampling.
- Be aware of sources of contamination on the sampling vessel (exhaust fumes, engine cooling systems, oily surfaces). Work up-wind of any exhausts. Segregate dirty/clean areas. Lay out clean substrates to work on and replace frequently.
- Collect background samples from clean sites representative of pre-oiling conditions, as well as areas not yet oiled but in the potential path of the oil.



- Preservation chemicals should be provided by the lab.
- Use a computer or conceptual model of the extent of water-column contamination to determine the number and location of samples. Minimum guidelines are at least three samples per area of relatively uniform exposure or sub-waterbody. Also, sample along exposure gradients, starting in the cleanest zone, at regular intervals proportional to the exposure area.

Contact James R. Payne at PEI for questions or additional information  
jrpayne@sbcglobal.net (760) 942-1015; cell 760-613-7391