

**Protocols for the Collection of Water, Sediment and Tissue Samples for Chemical
Analyses of Petroleum Hydrocarbons**

(Based on NOAA Damage Assessment Center
Rapid Assessment Program
Sampling Guidelines, 2002)

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Protocols For Collecting WATER SAMPLES

Sampling Objectives

- To determine the concentration of oil compounds in the water column. The method detection level (MDL) and sample size are critical in determining detection limits.
- To determine the source via fingerprinting, the degree of weathering, and background levels
- To document exposure of water-column organism and validate toxicity models.
- To maintain the integrity the sample(s) during sampling, transport, and storage.

Sample Volume (use this chart to select sample size to reach the desired detection limit)

<i>Analytical Method (see back page)</i>	<i>Sample Volume</i>	<i>MDL</i>	<i>Level of Toxicity Concern*</i>
BTEX (full scan mode)	40 ml	10 ug/L (ppb)	10 ug/L @ 25 C
BTEX (SIM)		0.1-1 ug/L	10 mg/L @ 2 C
THC by GC/FID	1 liter 1 gallon	2,000 ug/L 500 ug/L	N/A
PAH by GC/MS-SIM	1 liter 1 gallon	0.4 ug/L 0.1 ug/L	0.01 ug/L @ 25 C 2 ug/L @ 2 C

* defined as 1% of the LC50 for 96 hours for sensitive water-column species

Sampling Equipment/ Containers

- Collect samples directly into the sample container, to minimize risks of cross-contamination, either by hand or using a sampler which holds the container, if possible.
- 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.
- Collect BTEX samples in 40-mL VOA vials, filled with no headspace or air bubbles.
- If slicks are present, decontaminate samplers before each use. First wash with laboratory-grade detergent and clean water, with a triple clean water rinse (distilled water from a local store is OK). Then rinse with methanol or acetone, followed by methylene chloride or hexane (Capillary GC Pesticide Residue Grade or equivalent). Allow solvents to evaporate before use. Do not work with solvents downwind of exhaust or other airborne hydrocarbon source. Collect solvent rinsate for proper disposal or shipment to the lab as a rinsate blank.

Sample Collection Methods

- Collect subsurface samples below the water surface; so not to include any surface slicks.
- Take "near surface" samples from 0-1 m below the surface; take "near bottom" samples 1 m from the bottom.
- Sampling equipment MUST be deployed and retrieved in the closed position. Applies to sample jars lowered by hand. Open or un-cap the sampler only at the sampling depth.
- On each trip, try to sample the control and least oiled areas first, then more contaminated areas.
- Clear surface slicks prior to deploying the equipment, but carefully so that the surface oil is not dispersed into the water column. Sweeping the area with sorbents is effective.
- Preservation/Holding Times
- Volatiles (VOA vial): None. Can be held for 14 days at 4°C in the dark without loss of sample integrity.
- TPHs and PAHs: can add 1 ml, of 6 N HCl/liter of sample, but not required by EPA.
- Immediately place all water samples in cooler and keep at 4°C (do not freeze).
- Use packing material around containers to prevent breakage.
- Water samples can be held at 4°C in the dark for up to 7 d without loss of sample integrity. Water extracts can be held at 4°C in the dark for 40 days without loss of sample integrity.

Protocols For Collecting SEDIMENTS

Sampling Objectives

- To determine the concentration and source of oil compounds in the sediments collected.
- To measure sediment characteristics for interpreting chemical and biological results.
- To maintain the integrity the sample(s) during sampling, transport, and storage.

Sample Volume by Analytical Method

THC by GC/FID	500 ml; or 1 pint or 16 oz
PAH by GC/MS-SIM	500 ml; or 1 pint; or 16 oz
TOC	10 g; or less than 10 ml
Grain size	100 g; or 4 oz

Intertidal Sediments

Sampling Equipment / Containers

- To collect subsurface samples of coarse sediments (sand and gravel), it is easiest to use a shovel to dig a small trench and collect the desired sediment intervals from the exposed wall in the trench.
- To collect subsurface samples in fine sediments (mud), use a shovel to expose the sediments at the desired depth. Collect the sample from the natural break side, rather than the shovel side.
- Coring tubes can be used in muddy sediments when the sampling intervals have not been determined. Plastic tubes (polycarbonate or polyethylene is okay) should be 5 cm (2 in) in diameter, with a wall thickness of about 3 mm.
- Sediment samples for THC and PAH should be placed in glass containers, certified-clean to be organic-free (solvent rinsed), with Teflon or aluminum-lined lid. For TOC, they can be placed in soap-cleaned glass or plastic containers. For grain size, Ziploc or Whirl-Pak bags can be used.

Sample Collection Methods

- Decontaminate sampling equipment and supplies initially and between samples, if re-using them. First, wash with laboratory-grade detergent and clean water, with a triple clean water rinse. Use a clean water source for rinsing (distilled water from a local store is OK). Then rinse with methanol or acetone, followed by methylene chloride or hexane (Capillary GC Pesticide Residue Grade or equivalent). Do not work with solvents downwind of exhaust or other airborne hydrocarbon source. Collect waste/rinsate solvents for proper disposal
- To reduce the need for field decontamination, use pre-cleaned, disposable utensils (e.g., stainless steel blade or wooden spatula), single-use core tubes, etc. The only equipment to be used between sites is a shovel
- Discrete samples from a single sample point may be collected to represent a specific condition, such as a tarball for fingerprinting and source identification.

- Composite samples (of at least three subsamples) are recommended for characterization of a sampling site, such as contaminant content in marsh sediments.
- Photograph the sampling site prior to sample collection to document the site conditions.
- For surface sediments, use a wooden spatula or stainless steel blade to accurately collect the top 2 cm, avoiding contact with disturbed sediments.
- For subsurface sediments, expose a fresh surface at the desired interval, and then remove the sediments that were in contact with the shovel prior to sampling.
- On each trip try to sample the control and least oiled areas first, then the most contaminated areas.
- Record the sample no. on both the label and lid. Record the following on the field log sheet:
 - sample no.; date/time; station location; tidal elevation
 - description of oiling conditions, using standard shoreline assessment terminology
 - sediment characteristics: texture, color, biota, vegetation, debris, odor, etc.
- Make a quick sketch in a field logbook or sketch form showing the sampling locations in enough detail that the location could be re-occupied by someone else.

Subtidal Sediments

Sampling Equipment / Containers

- Any sediment sampling device which meets the following requirements can be used: - creates a minimum bow wake when descending - penetrates the sediments below the desired sampling depth - closes to form a leak-proof seal after the sediment sample is taken - prevents sediment washout and disturbance when ascending
- Common sampling devices include: modified van Veen grab; Ekman grab; box dredge.
- Sediment samples for THC and PAH should be placed in glass containers, certified-clean to be organic-free (solvent rinsed), with Teflon or aluminum-lined lid. For TOC, they can be placed in soap-cleaned glass or plastic containers. For grain size, Ziploc or Whirl-Pak bags can be used.

Sample Collection Methods

- In oiled areas, decontaminate all sampling equipment and supplies initially and between samples. First wash with laboratory-grade detergent and clean water, with a triple clean water rinse. In oiled areas, use a clean water source for rinsing (distilled water from a local store is OK). Then rinse with methanol or acetone,

followed by methylene chloride or hexane (Capillary GC Pesticide Residue Grade or equivalent). Do not work with solvents downwind of exhaust or other airborne hydrocarbon source. Allow solvents to evaporate before use. Collect waste/rinsate solvents for proper disposal

- Avoid contamination from surface slicks if present.
- Lower and retrieve sampling device at a controlled speed of approx. 1-foot per second.
- The device should contact the bottom gently; only its weight or piston mechanism should be used to penetrate the sediment. It is important to minimize the disturbance of the surface floc.
- Inspect the sample to make sure that it meets the following criteria: -the sampler is not overfilled; the sediment is not pressed against the sampler top. -overlying water is present, indicating minimal leakage. -sediment surface is undisturbed, indicating lack of channeling or sample washout -the desired penetration depth is achieved (e.g., 4-5 cm for a 2 cm sample.)
- Siphon off the overlying water near one side of the sampler.
- Using a flat scoop, accurately collect the top 2-cm, avoiding sediments in contact with the sides of the sampler. Use a new scoop for each station. Collect other intervals, per the sampling plan.
- Each sample should be a composite collected from three deployments of the sampler at a station
- On each trip, try to sample the control and least oiled areas first, then the most contaminated areas.
- Record the sample no. on both the label and lid. Record the following on the field log sheet:
 - sample no.; date/time; location; water depth; penetration depth; surface sediment characteristics: texture, color, biota, debris, sheens, odor, etc.;
 - vertical changes in sediment characteristics.

Preservation/Holding Times

- Immediately place all sediment samples in a cooler and keep at 4 C. Freeze samples for chemical analysis by the end of each day. Refrigerate samples for TOC and grain size (do not freeze).
- Use packing material such as bubble wrap, around containers to prevent breakage.
- Sediment samples can be held frozen in the dark for several years without loss of sample integrity.
- Sediment extracts can be held at 4°C in the dark/or 40 days without loss of sample integrity.

Protocols For Collecting SHELLFISH TISSUES

Sampling Objectives

- To document extent and duration of the area exposed to the spilled material. Bivalves uptake oil quickly, depurate them slowly, and can be used as "composite" samplers.
- To determine the spill source via fingerprinting analysis.
- To assess the risk to organisms from consuming contaminated prey.
- To document the bioavailability and exposure pathways of the spilled material.
- To maintain the integrity the sample(s) during sampling, transport, and storage.

Sample Size

PAH by GC/MS-SIM	30 g wet weight (composite of -20 individual organisms)
Lipid and Water Content	A sub-set of the sample is used for these analyses

Sampling Equipment/Containers

- Dredges, tongs, or grabs are used to collect shellfish from subtidal areas. Shovels are used to dig up infaunal shellfish from intertidal areas. A screen is useful for sieving sediments.
- If oil is present, decontaminate dredges, knives, etc. between samples. First wash with laboratory-grade detergent and clean water, with a triple clean water rinse (distilled water from a local store is OK). If the equipment is obviously contaminated, rinse with methanol or acetone, followed by methylene chloride or hexane (Capillary GC Pesticide Residue Grade or equivalent). Let solvent evaporate before use. Do not work with solvents downwind of exhaust or other airborne hydrocarbon source. Collect solvent rinsate for proper disposal.

Sample Collection Methods

- Attached organisms are pried away from the substrate with a knife, trowel, etc. Infaunal samples should be rinsed with site water to remove sediments. Collect primarily live animals (shells intact and tightly closed). Note the condition of dead animals if they are appropriate for collection. Photograph all collection sites prior to sampling.
- The sampler handling the shellfish should wear surgical gloves and change gloves after each sample. Record observations of any external evidence of contamination.
- Composite samples are recommended to provide enough sample weight to meet detection limit objectives and to average out the variations at a location among

individual organisms. If uncertain about the number of individuals needed to meet minimum weight requirements, open, shuck, and weigh individuals of a certain size for calibration.

- Individuals should be the same shell (or body) size. Record size range collected or save shells for later measurement. Same size is not as important if only for fingerprinting.
- Shellfish should not be opened in the field to minimize the risk of contamination. Rather, sets of whole organisms are wrapped together in clean aluminum foil. Rinse the foil with methanol or acetone, then rinse again with methylene chloride or hexane (Capillary GC Pesticide Residue Grade or equivalent). Collect solvent rinsate for proper disposal.
- Wipe oiled shells with sorbent pads, wipes, etc. If heavily oiled, use a solvent on the wipe.
- Place all individuals of the same species from a site in a glass jar or double Ziploc bags.
- A waterproof sample label is placed between the two bags or on the sample jar and lid.
- Sample the control and least oiled areas first, then sample the more contaminated areas.
- Use packing material around containers to prevent breakage during handling and shipping.

Preservation/Holding Times

- Immediately place all samples in cooler and keep at 4°C. Freeze as soon as possible. Once properly frozen, they can be held for years without loss of sample integrity.

Personnel

The personnel below are likely to be contacted by the State of RI if the RIOST is activated in the event of an oil spill in RI waters. It is certainly not a final list, but rather a list of those individuals who have indicated a willingness to help in the collection of samples for chemical analyses. The actual chemical analyses of the samples will be done by a contractor selected by the State of RI.

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Equipment

Solvent cleaned Go-Flo Bottles will be needed to collect the water column samples , clean dredges/tongs/grabs will be needed for the shellfish samples and solvent cleaned utensils will be needed for the sediment samples. In addition, solvent cleaned bottles for storage of water samples, jars for sediment samples and aluminum foil for shellfish tissue samples will be required. The chemicals required will include high purity organic solvents(hexane, methanol and methylene chloride), and acids(HCl). Boat time will be needed for the collection of water samples and shellfish samples. and refrigerator/freezer space will be needed for the storage of samples before and after analyses.

Budget

The estimated budget for the collection of the above samples is about \$ 5,000 to \$10,000 for purchase of sampling gear(Go-Flo Bottles), storage containers and chemicals, depending on what currently available at the GSO/URI and RIDEM. Refrigerator and freezer space is probably available in several laboratories at the GSO, but security of these facilities will have to be checked. The budget assumes that funds for ship time as well as associated equipment (e.g., dredges) will be made available by RIDEM.