

Protocols For Collecting NRDA Samples

SUBTIDAL SEDIMENTS

Sampling Objectives

- To determine the concentration and source of oil compounds in sediments.
- To measure sediment characteristics for interpreting chemical and biological results.
- To document the presence or absence of sunken oil.

Sample Volume by Analytical Method (*see back page for description and suggested detection limits*)

AHC by GC/ FID	250 mL; or 1/ 2 pint; or 8 oz
PAH by GC/ MS-SM	1/ 2 pint; or 8 oz (same sample as above)
TOC	10 g ; or 10 mL
Grain size	100 g; or less than 4 oz (separate sample)

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 AHC and PAH should be placed in glass containers, certified-clean to be organic-free (solvent rinsed), with Teflon- or aluminum foil-lined lids. 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

- Decon all sampling gear before using and between sampling stations. First wash with laboratory-grade detergent and clean water.
- In oiled areas, decon all sampling equipment and supplies between samples.
- Avoid contamination from surface slicks if present.
- Lower and retrieve the sampling device at a controlled speed of ~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 disturbance to the surface floc which is likely to contain oil contaminants.
- Inspect the sample to make sure that it meets the following criteria:
 - the sampler is not overfilled; the sediment surface 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.
- On each trip, try to sample control and least oiled areas first, then the most contaminated areas.
- A field/ trip blank should be prepared by opening a sample container (jar) and allowing it to stand open for the time it takes to collect field samples (3-5 minutes). Ideally, kiln-fired sand supplied by the laboratory can be transferred (poured or scooped) from one container to another and returned to the lab as a field blank, but if this is not possible, the open jar technique is acceptable.

- Record the sample no. on both the label and lid. Record the following on the field log sheet: sample no.; date/ time; location; gps coordinates, 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 for 40 days without loss of sample integrity.

Analytical Methods

- Aliphatic hydrocarbons** (SHC or AHC). Often referred to as total petroleum hydrocarbons, but most methods do not differentiate among petroleum, pyrogenic, and biogenic hydrocarbons. AHC 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 (2 ppm versus 100-1000 ppm for other THC methods) and the direct measurement of hydrocarbons. This method does not detect low boiling compounds (below $n-C_8$). For NRDA, AHC 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 AHC results, however, can be used to track oil weathering and map extent of exposure to benthic resources. Detection limits are usually higher than those needed for benthic injury assessment. Sample prep may require extra steps to remove lipids which may interfere with the analysis.
- Polycyclic aromatic hydrocarbons** (PAH). Since most of the toxicity in oil is due to the PAHs, it is often the preferred analysis for NRDA. The analytes must 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 mode. Detection levels should be 1 ppb for individual PAHs to support injury assessment using toxicity thresholds. **Important:** Have the lab also run the source oil.
- Biomarkers (S/T)**. Sterane/ triterpane biomarkers are “fossil” compounds unique to the oil formation that are very resistant to weathering, persisting for decades after some events. These compounds provide a secondary and confirming line of evidence in forensic oil identification. These data are also generated by the 8270 method.

Other Considerations

- 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.
- Use a physical or mental model of the extent of benthic contamination to determine the number and location of samples. Minimum guidelines are at least three samples per area of relatively uniform exposure or distinct waterbody. Also, sample along exposure gradients at regular intervals proportionate to the exposure area.
- Present chemical results on a dry-weight basis.
- Collect separate splits for infauna or bioassay, so they can be correlated with chemical results.

Key References

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