

Protocols For Collecting NRDA Samples

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 organisms 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 µg/L (ppb)	10 µg/L @ 25°C
BTEX (SIM)		0.1-1 µg/L	10 mg/L @ 2°C
THC by GC/FID	1 liter	2,000 µg/L	N/A
	1 gallon	500 µg/L	
PAH by GC/MS-SIM	1 liter	0.4 µg/L	0.01 µg/L @ 25°C
	1 gallon	0.1 µg/L	2 µg/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, decon 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 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 control/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.
- TPH and PAH: 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.

Analytical Methods

- **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 or full scan mode to include the alkylated 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 hydrocarbons. This method does not detect low boiling compounds (below $n-C_8$). 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.
- **Polynuclear 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 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.
- Acquire preservation chemicals locally; acids have special hazmat shipping requirements.
- Use a physical or mental 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 at regular intervals proportionate to the exposure area.

Key References

- NOAA, 1993. Sampling and analytical methods of the National Status and Trends Program, National Benthic Surveillance and Mussel Water Projects, 1984-1992. Volume IV, Comprehensive descriptions of trace organic analytical methods. Lauenstein, G.G. and A.Y. Cantillo (eds.). NOAA Tech. Memo NOA ORCA 71, Silver Spring, MD. 181 pp.
- Sauer, T.C. and P.D. Boehm, 1995. Hydrocarbon chemistry for analytical methods for oil spill assessments. Marine Spill Response Corporation Technical Report Series 95-032, Washington, D.C. 114 pp.
- USEPA, 1979. Methods for chemical analysis of water and wastes. EPA-600/4-79/020. USEPA Environmental Monitoring Systems Laboratory, Office of Research and Development, Cincinnati, Ohio.
- USEPA, 1986. Test methods for evaluating solid waste. SW 846 Third Edition (and updates).