Washington State Department of Ecology

Spill Prevention, Preparedness, & Response Program

Standard Operating Procedure for Collecting Oil Spill Intertidal Sediment Samples

Version 1.0

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Signatures on File

Please note that the Washington State Department of Ecology's Standard Operating Procedures (SOPs) are adapted from published methods, or developed by in-house technical and administrative experts. Their primary purpose is for internal Ecology use, although sampling and administrative SOPs may have a wider utility. Our SOPs do not supplant official published methods. Distribution of these SOPs does not constitute an endorsement of a particular procedure or method.

Any reference to specific equipment, manufacturer, or supplies is for descriptive purposes only and does not constitute an endorsement of a particular product or service by the author or by the Department of Ecology.

Although Ecology follows the SOP in most instances, there may be instances in which Ecology uses an alternative methodology, procedure, or process.

SOP Revision History

Revision Date	Rev number	Summary of changes	Sections	Reviser(s)
09-30-2011	1.0			

Washington State Department of Ecology

Spill Prevention, Preparedness, & Response Program

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1.0 Purpose and Scope

1.1 This document is the Spill Prevention, Preparedness, & Response (Spills) Program Standard Operating Procedure (SOP) for collecting oil spill intertidal sediment samples.

1.2 **Objectives** – 1) To determine the concentration of oil compounds in intertidal sediment. 2) To document exposure of organisms present in intertidal sediment and validate toxicity models. 3) To maintain the integrity of the sample(s) during sampling, transport, and storage.

1.3 The main purpose for collecting oil spill intertidal sediment samples is to document the concentrations of oil compounds in the sediment and exposure of natural resources to determine if the resources have been injured. To be legally valid, samples must be carefully collected to prevent contamination and strict chain-of-custody must be maintained throughout collection, transport, and analysis.

1.4 Two analyses are typically conducted on intertidal sediment samples collected for oil spills; Total Petroleum Hydrocarbons (TPH) and Polynuclear Aromatic Hydrocarbons (PAHs). Detection limits for TPH analyses are usually higher than those needed for intertidal sediment injury assessment, but the cost of this analysis is much lower than the PAH analysis and TPH can be used to track oil weathering and map extent of exposure of intertidal resources if the budget for analyses is limited. PAHs are very persistent and cause most of the chronic toxicity, and are therefore the preferred analysis for NRDA injury assessment.

2.0 Applicability

2.1 This procedure is based on protocols developed by Research Planning, Inc. (http://www.researchplanning.com/services/damage-assessment-restoration/) for NOAA for oil spill Natural Resource Damage Assessments (NRDA). The protocols were based on sampling and analytical methods developed for the National Status and Trends Program. These protocols are widely accepted and used by oil handling companies, consultants, and other trustees and should be used for all oil spill related sampling.

3.0 Definitions

3.1 NOAA – National Oceanic and Atmospheric Administration.
3.2 GC/FID – Gas Chromatograph/Flame Ionizing Detector
3.3 GC/MS – Gas Chromatograph/Mass Spectrometer

3.4 TOC – Total Organic Carbon
3.5 TRAP – Trustee Resource Assessment and Protection.
3.6 NRDA – Natural Resource Damage Assessment.
3.7 SOSC – State on Scene Coordinator

4.0 Personnel Qualifications/Responsibilities

4.1 Any Ecology employee that expects to collect oil spill related samples must attend appropriate training from a Spills Program Sampling Specialist. Oil spill intertidal sediment sample collection can be conducted by any employee that has completed basic and intermediate sampling training and has collected at least one quantitative field sediment sample under the supervision of an experienced sampler. All Spills Program employees (including managers and administrative staff) are encouraged to attend basic sampling training. Due to safety requirements, at least two people are recommended for any field sampling and anyone that has taken the training, with or without field experience, can assist an experienced sampler.

5.0 Equipment, Reagents, and Supplies

5.1 Equipment

5.1.1 Samples should be collected in certified clean glass containers. Alternatively, new glass containers (such as Mason jars or uncertified jars) can be used if certified containers are not available, but at least one empty container should be submitted with the samples as a container blank. Metal containers, such as stainless steel bowls or buckets, can be used to collect the samples if necessary as long as they are thoroughly cleaned first, but the samples should be transferred to glass containers for shipment to the laboratory. Plastic containers should never be used (except for samples collected for grain size analysis).

5.1.2 Intertidal sediment is collected in one-liter (32 oz.) wide-mouth jars (with Teflon lined caps) and is transported to a sample processing center (laboratory or clean-room) where the sediment is homogenized and split into the required containers for analysis.

5.1.3 The laboratory that performs the analyses may also homogenize and split the samples (usually for an additional fee). If not, a four quart pre-cleaned stainless steel bowl and a pre-cleaned stainless steel spoon will be needed for sample homogenization and splitting. Split samples are transferred into 8 oz. and 4 oz. pre-cleaned wide-mouth glass jars with Teflon lined caps (samples collected for grain size analysis can be placed in 4 or 8 oz. plastic jars).

5.1.4 GPS (set datum to WGS-84, Latitude/Longitude to decimal degrees).

5.1.5 Digital camera (synched to GPS time).

5.1.6 Ice chests with wet or blue ice (preferably equipped with chain of custody security cables).

5.2 **Reagents**

5.2.1 Pesticide grade acetone and hexane for decontamination.

5.3 **Supplies**

5.3.1 Sample tags and labels
5.3.2 Field notebook
5.3.3 Chain-of-custody seals
5.3.4 Chain-of-custody forms
5.3.5 Nitrile disposable gloves
5.3.6 Ziploc bags
5.3.7 Paper towels
5.3.8 Stainless steel spoons or spatulas
5.3.9 Liquinox or equivalent soap
5.3.10 Aluminum foil
5.3.11 Cleaning brush
5.3.12 Distilled water

6.0 Summary of Procedure

6.1 **Sample Collection Procedure**

6.1.1 Safety is of greatest concern. Be aware of physical and chemical hazards at the site. Get a safety briefing before entering the area. Do not enter confined spaces unless they have been determined to be safe. Use recommended safety equipment and procedures.

6.1.2 Develop a sampling plan. Identify the number and type of samples that are to be collected, the type of containers that will be used, and unique identifiers for each sample. Make a drawing of the area being sampled, including points of reference and the location of each site where samples are collected so the sites could be located later if necessary. Identify the sampling procedure(s) that will be used. Include any preservation techniques used for the samples, the type of analyses that will be done, and the laboratory that the samples will be sent to. The plan can be recorded in a field notebook or on a separate piece of paper; there is no required form or specific format that must be followed. Each plan will be different depending on the number and type of samples being collected and the complexity of sampling site.

6.1.3 Intertidal sediment is collected in one-liter (32 oz.) clear wide-mouth jars and is transported to a sample processing center (laboratory or clean-room) where the sediment is homogenized and split into the required containers for analysis. Alternately, the sediment can be homogenized in the field (see 6.1.4). For each sample, use a pre-cleaned stainless steel spoon to collect the top 2 cm of sediment in an undisturbed area. Continue collecting spoonfuls (sub-samples) randomly from an area about one-meter in diameter until the jar (or bowl) is at least ¾ full. Do not fill the jar to the top; leave at least ¾ inch for expansion in case the sample needs to be frozen. In

areas covered with coarse material (rocks, cobble, etc.), remove the coarse material so the underlying fine-grained material is exposed. The latter is then collected for the sample. Rocks and debris larger than about ½ inch (1 cm) in diameter should be discarded.

6.1.4 The laboratory that performs the analyses may also homogenize and split the samples. If not, the sediment for a sample is dumped into a four quart pre-cleaned stainless steel bowl, stirred with a pre-cleaned stainless steel spoon until the sample appears to be homogenous, and then transferred into two 8 oz. wide-mouth jars (TPH and PAHs), and two 4 oz. wide-mouth jars (TOC and grain size). Fill the jars ¾ full.

6.1.5 Avoid freezing the samples in the one-liter jars before homogenization and splitting. Sediment used for grain size analysis should not be frozen.

6.1.6 Label each container with an adhesive label directly applied to the container and with a paper tag attached to the container with an elastic band. Use a waterproof pen or marker to record the project or incident name, a station identifier, a unique sample identifier, the collection date and time, the desired analysis type (TPH, PAH, etc.), and the sampler's name or initials on each label. The adhesive label should be filled out and applied to the container prior to sample collection.

6.1.7 After labeling, place each sample container in a separate Ziploc bag to reduce the chance of contamination should a container leak or break.

6.1.8 Immediately place all samples in a cooler and keep at ≤6°C. If necessary, all samples except the grain size sample can be frozen.

6.1.9 Use packing material, such as bubble wrap, around containers to prevent breakage.

6.1.10 Fill out the chain-of-custody form; be sure to record all information for each sample. Record the same information in a field notebook and add specific information about where each sample was collected from, including latitude-longitude, the depth the sediment was collected from, and a map if necessary. Also include the sampling devices used, container sizes and types, if any preservative was used, and sampler name.

6.1.11 Make special notation on the chain-of-custody form about any problems or observations during sampling, such as potential sources of contamination, etc.

6.1.12 Maintain strict chain-of-custody during sample storage and transportation.

6.1.13 If possible, ship source samples separately from environmental samples to reduce risk of cross contamination.

6.1.14 PAH and TPH sediment samples can be held at ≤6°C in the dark for up to 14 days without loss of sample integrity. If samples are extracted within 14 days, the holding time for the extracts is 40 days. The holding time for frozen PAH sediment samples is 1 year if held at ≤-18°C. The holding time for TOC is 14 days if held at ≤6°C or 6 months if frozen.

6.2 **Analytical Methods**

6.2.1 **Total Petroleum Hydrocarbons** (TPH). As the name implies, this analysis is used to estimate the total amount of petroleum hydrocarbons in a sample, but does not differentiate among petroleum, petrogenic, and biogenic hydrocarbons. TPH can be used as an inexpensive alternative to the PAH analysis to monitor weathering and document the extent of exposure, but is not adequate for providing the data needed to support calculation of toxic effects and detection limits are usually not low enough for aquatic injury assessment. This analysis is called NWTPH-Dx (diesel extended range) at the Manchester Laboratory and a GC/FID is used to quantify all hydrocarbons other than gasoline range compounds.

6.2.2 **Polynuclear Aromatic Hydrocarbons** (PAH). PAHs are used to characterize the spilled oil, monitor weathering, and predict toxicity. 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 (NOAA list), because the list of PAHs is expanded to include the alkylated homologs, using GC/MS in the selected ion monitoring (SIM) mode.

6.3 **Decontamination Procedure**

6.3.1 Wash with soap (Liquinox or equivalent) and water (preferably hot), scrubbing all surfaces thoroughly with the cleaning brush. If the item being cleaned is heavily contaminated (oiled), this step should be repeated after washing to remove gross contamination.

6.3.2 **Procedure**:

6.3.2.1 Rinse with tap water and then triple rinse with distilled water.
6.3.2.2 Rinse with acetone.
6.3.2.3 Rinse with hexane.
6.3.2.4 Allow to air dry.
6.3.2.5 If item is not used immediately, wrap in solvent rinsed aluminum foil.

7.0 Records Management

7.1 Sampling Plan Template – Use this form as an aid for developing a complete and comprehensive sampling plan. This form is not required for developing a sampling plan, but provides ready access to guidelines and reminders.

7.2 Sampling Documentation Form – Use this form as an aid and reminder for recording complete and comprehensive sampling information, and to provide a single place to record information for multiple samples.

7.3 Both forms are available at:
http://teams/sites/SPPR/response/trap/Sampling/Forms/AllItems.aspx (SharePoint)
or X:\Spills_Program\Response Section\TRAP-NRDA\Sampling\

7.4 Oil Spill Chain-of-Custody Form (ECY 050-42 (11/01))

8.0 Quality Control and Quality Assurance Section

8.1 There are no QA/QC requirements specific or unique to this procedure. Field splits should be avoided, unless the samples are collected in bowls and split into separate containers in the field. If splits are requested, the samples should be submitted to the laboratory and the laboratory can be asked to split the samples. Typically, the laboratory will extract the samples and then split the extracts. The laboratory will usually provide splits directly to the requester or their laboratory if the sample contains enough material.

9.0 Safety

9.1 Sample collection can present some unusual circumstances that could have equally unusual associated safety hazards. Samplers should consult with the Safety Officer or SOSC and review the incident safety plan or Hazard Assessment Worksheet (HAW) prior to developing a sampling plan so known hazards can be avoided. Samplers should also be aware that sampling will often take place in areas that may not be adequately addressed in the safety plan or HAW. If there is any question, then a separate HAW should be prepared prior to sampling. A Sampling HAW is available at: http://teams/sites/SPPR/response/trap/default.aspx (SharePoint) or X:\Spills_Program\ Response Section\TRAP-NRDA\Sampling, that includes action levels appropriate for sampling various petroleum products.

9.2 Some hazards that could be associated with sampling are:
9.3 Low areas that could collect fumes (vapors) or have reduced oxygen levels (confined space)
9.4 Higher concentrations of fumes at ground level where samples are collected
9.5 General water hazards when collecting samples on a shoreline or from a boat or dock, etc.
9.6 Increased risk of slips, trips, and falls
9.7 Traffic when sampling near a highway
9.8 Dangerous animals
9.9 Exposure to elements (hot or cold)
9.10 Eye damage from splashes or brush/branches

10.0 References

10.1 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 NOS ORCA 71, Silver Spring, MD. 181 pp.